t: DEVELOPMENT OF ADHESIVES FOR
VERY LOW TEMPERATURE APPLICATION

FINAL SUMMARY REPORT *C 10 Apr.1961 - 10 Apr.1963]*
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Engineering Materials Branch
Propulsion and Vehicle Engineering Division
National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama

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FOREWORD

This report was prepared by Narmco Research & Development, - Division of Telecomputing Corporation, under Contract NAS 8-1565, "Development of Adhesives for Very Low Temperature Application," to the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the direction of the Engineering Materials Branch, Propulsions and Vehicle Engineering Division of the George C. Marshall Space Flight Center with Mr. C. M. Holmes acting as project manager. The research effort was begun on 10 April 1961 and continued to 10 April 1963.

ABSTRACT

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A literature survey was conducted on adhesives for cryogenic applications. This survey was augmented with specific tests of commercially available adhesives which had been reported as serviceable at low temperature. The results of the survey and adhesive evaluation were used to guide the research efforts for improved field use adhesives for cryogenic applications.

Research efforts were concentrated in the areas of nylon-epoxy, epoxy-polyamide, polyurethane, and fluorocarbon film systems. Effects of fillers, film supporting media, and surface preparation were evaluated. A wide variety of aluminum and stainless alloy adherends were also evaluated. Tensile shear, tee peel, mechanical shock, and butt tensile strengths were determined down to -423°F. Impact, compression loading, and coefficients of expansions were determined down to -320°F.

The best six adhesives were   1) a nylon powder filled epoxy-polyamide paste system,   2) a Teflon FEP film epoxy-polyamide composite, 3) and 4) polyurethanes, 5) a glass fabric supported polyurethane, and 6) a Teflon FEP hot-melt adhesive. With the exception of the latter, all adhesives were capable of producing bonds when cured at ambient temperature and contact pressure. The adhesives can provide 1) excellent moderate low-temperature strength properties, 2) excellent low-temperature strength properties, 3) excellent low-temperature strength and toughness properties, 4) excellent low-temperature strength and toughness with fast cure, 5) superior peel strength at extremely low temperature, and 6) excellent strength and toughness at very low temperature, respectively. Only Teflon FEP hot-melt adhesive exhibited LOX compatibility. Complete specifications for each adhesive are included in this report.

AUTHOR

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I. INTRODUCTION

A. Objective and Purpose

The purpose of this program was to provide the National Aeronautics and Space Administration with an adhesive, or family of adhesives, for bonding clips, brackets, etc., to skin portions of fuel and oxidizer containers and other related components of launch vehicles for space craft. The adhesives were to be applicable w' en completely submerged in cryogens such as liquid oxygen, liquid nitrogen, and liquid hydrogen. It was desired that the techniques of surface preparation and bonding be simple and readily adaptable to field use by technicians having little or no experience in plastics technology. It was further desired that the adhesive be suitable for application to vertical, horizontal, or overhead surfaces. Bonding and curing were to be accomplished under ambient conditions with an absolute minimum of bonding pressure -- less than 1 psi.

Further requirements of the adhesive were to be resistance to environmental exposure, high thermal conductivity, low shrinkage, thermal expansion matched to that of adherend, modulus equal to or lower than adherend, high strength, low specific gravity, long shelf life, short cure time, tape form, sufficient flow to fill voids, thermosetting, high impact and peel resistance, good aging resistance, mechanical shock and vibration resistance, and that they be applicable over the -423 to +260°F temperature range.

B. Narmco Concept of Adhesives for Cryogenic Application

At extremely low temperature, the physical properties and behavior of atoms and molecules are drastically altered. In polymers, molecular motion is restricted and the ability of the molecules to move produces extreme brittleness. When an external force is applied, the energy is prematurely absorbed by valence bond rupture, and the adhesive fails. Silicone rubbers and fluids have been used at low temperatures because of a favorable viscosity-temperature relationship; it is ability of the methyl groups to rotate freely about the silicon atom that prevents the development of extreme brittleness, although the rate of rotation is slowed. Silicone polymers are amorphous or non-crystalline materials. This property is an aid to freer molecular motion.

Very few structural adhesives are either completely crystalline or completely amorphous, so various degrees of crystallinity do exist. Organic polymers which lack ionic bonding have cross linkages which act to support the strength of the covalent bonds. Unfortunately, the cross linkages also serve to increase brittleness and decrease toughness. A compromise for this problem is found in a weaker type of crosslinking bond, called the hydrogen bond. A hydrogen bond has a dissociation energy of about 2-5 Kcals/mole compared to about 50 Kcals/mole for a C-C bond. If hydrogen bonds, or bonds of similar strength, can be incorporated in sufficient numbers as cross-linkages, their action could result in desirable properties at normal temperatures and impart to the adhesive the necessary strength at very low temperatures, without the penalty of brittleness produced by covalent crosslinkages. As an example, nylon has all these attributes. When incorporated into an adhesive containing an epoxy polymer, the

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effects are most beneficial at cryogenic temperatures. The adhesive system is now preponderantly amorphous, and so its brittleness is reduced and application of an external force fails to severely break covalent bonds.

Another important phenomenon now enters: applied forces align the nylon molecules, which allows the energy to be absorbed, the result being favorable orientations to permit formation of hydrogen bonding. This not only provides an energy sink which might be termed an energy of orientation, but the hydrogen bond formation adds large numbers of weaker cross links and strengthens the adhesive. This is not an instantaneous process, so a single application of a tensile force does not completely orient all the nylon molecules. It is for this reason that the adhesive does not embrittle rapidly.

In general, then, our basic thoughts toward development of adhesives for extremely low temperature applications include hydrogen bonding for preventing low temperature embrittlement, adhesive processing techniques to prevent low temperature embrittlement from residual solvents, filling and alloying techniques in adhesive formulation to control such factors as softening point and thermal expansion, and other areas as outlined in the text below.

C. Method of Approach

The following areas were studied in the attempt to develop improved adhesive systems for application at very low temperature:

1. Literature survey
2. Existing adhesive type selection
3. Metal surface treatments
4. Processing for nylon-epoxy adhesives
5. Nylon polymer and copolymer chemical structure
6. Modified nylons
7. New nylon-epoxy polymers
8. Comparison of epoxy with other resins for reinforcing nylon
9. Fillers
10. RT-cured epoxy-polyamine and epoxy-polyamide systems
11. Composite adhesives
12. Miscellaneous elastomers and resins
13. Polyurethane and modified systems
14. Fabric supported adhesives
15. Teflon FEP as a hot-melt adhesive
16. Chemical and physical improvements for adhesives
17. LOX impact insensitive adhesives

II. LITERATURE SURVEY

In order to establish the best possible foundation for carrying out a materials development program designed to produce a very low temperature adhesive, it was considered necessary to survey the available literature pertaining to the subject. It was intended that existing data serve as guides for future development, and that the literature survey be maintained on a continuing basis throughout the program to keep the research effort abreast of new materials and methods.

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The survey was conducted, and all available information on the performance of existing commercial structural adhesives in the cryogenic environment was collected. This included <u>Chemical Abstracts</u> (years 1948 to 1958 inclusive), new texts, private company reports, articles, and all Government reports and publications dealing with structural adhesives and plastics. In addition the manufactures of adhesives recommended for extremely low temperature application were contacted and their data were used extensively.

To date, Table 1 represents the most complete compilation of all existing data for commercial adhesives in cryogenic environments published under one cover. Thirty-one adhesives are represented from 18 different data sources. The data include those already published as well as data developed specifically under this contract to complete the areas for adhesives where no data existed.

III. EXISTING ADHESIVE TYPE SELECTION

Before any development work could be undertaken, it was necessary to establish the performance characteristics of the best available materials. The literature survey helped form the basis for the selection of existing commercial adhesives, along with the adhesive requirements listed in the Introduction. (Other requirements included ease of surface and bond preparation, thermosetting, and good aging characteristics.)

Figure 1 is a bar graph comparing the $-320°F$ tensile shear strength (metal-to-metal adherends) for a broad family of adhesives. The nylon-epoxy family was accordingly selected because of superior strength at low temperature. The epoxy-polyamide family was selected because of ease of bond preparation and moderate curing procedures. The polyurethane family was selected because of an actual gain in strength from room temperature to $-320°F$. The following is the list of commercial adhesives which were selected:

Adhesive	Type
Metlbond 406	Nylon-epoxy
Metlbond 408	Nylon-epoxy
AF-40	Nylon-epoxy
AF-41	Nylon-epoxy
FM-1000	Nylon-epoxy
Resin 3135*	Epoxy-polyamine
EC-1933B/A	Epoxy-polyamine
APCO-1261	Polyurethane

All other adhesive systems were excluded for one or more of the following reasons: their mediocre strength properties, their loss of strength in the cryogenic environment, or their relatively elaborate procedures for surface and bond preparation.

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*This, and all subsequent references to Resin 3135, refers to Resin 3135 with Curing Agent 7111.

	Adhesive and Manufacturer	Type	Cure	Adherend	+250°F	+180
1.	Metlbond 406, NO PRIME, Narmco Materials Div., Telecomputing Corp.	Nylon-epoxy	RT-350°F in 20 min, 1/4 Hr 350°F 25 psi.	.064" 2024T3 Clad .020" " " .064" 2024T3 Bare .064" 7075T6 Bare .020" " " .100" 5456 Bare .020" EFH 301 S/S .020" A-110-AT Ti	2000[9a] -- -- -- -- -- -- --	3860[7] -- -- -- -- -- -- --
2.	Metlbond 408, NO PRIME, Narmco Materials Div., Telecomputing Corp.	Nylon-epoxy	RT-350°F in 20 min, 1 Hr 350°F 25 psi.	.064" 2024T3 Clad .020" " " .064" 7075T6 Bare .020" " "	-- -- -- --	3110[10] -- -- --
3.	AF-40, NO PRIME, Minnesota Mining & Manufacturing Co.	Nylon-epoxy	RT-350°F 10°F/min, 1 Hr 350°F 50 psi.	.064" 2024T3 Clad .032" " " .064" 7075T6 Bare .020" " " .020" EFH 301 S/S	2900[11] -- -- -- --	4080[11] -- -- -- --
4.	AF-41, NO PRIME, Minnesota Mining & Manufacturing Co.	Nylon-epoxy	RT-350°F 10°F/min, 1 Hr 350°F 50 psi.	.064" 2024T3 Clad .032" " " .064" 7075T6 Bare .020" " "	-- -- -- --	3135[12] -- -- --

re	Adherend	Tensile Shear Strength, psi									Tee Peel Stre		
		+250°F	+180	RT	-40	-67	-90	-100	-320	-423	+250°F	+180	RT
in 20 min, 0°F 25 psi.	.064" 2024T3 Clad	2000_{9a}	3860_7	5980_7	--	5620_7	--	--	4360_a	--	--	--	--
	.020" " "	--	--	--	--	--	--	--	--	--	--	49.6_{9a}	60-70
	.064" 2024T3 Bare	--	--	5790_1	--	--	--	5470_1	5050_1	4580_1	--	--	--
	.064" 7075T6 Bare	--	--	--	--	--	--	--	4840_8	3813_8	--	--	--
	.020" " "	--	--	--	--	--	--	--	--	--	--	--	--
	.100" 5456 Bare	--	--	4110_{18}	--	--	--	--	--	--	--	--	--
	.020" EFH 301 S/S	--	--	5810_1	--	--	--	7790_1	6020_1	6730_1	--	--	--
	.020" A-110-AT Ti	--	--	4160_1	--	--	--	6110_1	5230_1	3440_1	--	--	--
in 20 min, F 25 psi.	.064" 2024T3 Clad	--	3110_{10}	6490_{10}	--	6480_{10}	--	--	2800_{9d}	--	--	--	--
	.020" " "	--	--	--	--	--	--	--	--	--	--	--	50-6
	.064" 7075T6 Bare	--	--	--	--	--	--	--	4090_8	2004_8	--	--	--
	.020" " "	--	--	--	--	--	--	--	--	--	--	--	--
10°F/min, F 50 psi.	.064" 2024T3 Clad	2900_{11}	4080_{11}	5000_{11}	6800_{11}	5800_{11}	5800_{11}	--	--	--	59_{11}	90_{11}	118_1
	.032" " "	--	--	--	--	--	--	--	--	--			
	.064" 7075T6 Bare	--	--	--	--	--	--	--	5990_8	5743_8	--	--	--
	.020" " "	--	--	--	--	--	--	--	--	--	--	--	--
	.020" EFH 301 S/S	--	--	3050_1	--	--	--	8550_1	5480_1	5200_1			
10°F/min, F 50 psi.	.064" 2024T3 Clad	--	3135_{12}	5700_{12}	--	6600_{12}	--	--	--	--	--	--	--
	.032" " "	--	--	--	--	--	--	--	--	--	--	71_{12}	111_1
	.064" 7075T6 Bare	--	--	--	--	--	--	--	5010_8	3402_8	--	--	--
	.020" " "	--	--	--	--	--	--	--	--	--			

:URE SURVEY

EXISTING COMMERCIAL ADHESIVES IN CRYOGENIC ENVIRONMENTS

e Shear Strength, psi						Tee Peel Strength, lbs/1"								Peel Rate
40	-67	-90	-100	-320	-423	+250°F	+180	RT	-40	-67	-90	-320	-423	in/min
-	5620[7]	--	--	4360[a]	--	--	--	--	--	--	--	--	--	
.	--	--	--	--	--	--	49.6[9a]	60-70[9a]	--	26.6[9a]	--	--	--	2
-	--	--	5470[1]	5050[1]	4580[1]	--	--	--	--	--	--	--	--	
.	--	--	--	4840[8]	3813[8]	--	--	--	--	--	--	--	--	
-	--	--	--	--	--	--	--	--	--	--	--	8.33[8]	8.2[8]	2
-	--	--	--	--	--	--	--	--	--	--	--	--	--	
-	--	--	7790[1]	6020[1]	6730[1]	--	--	--	--	--	--	--	--	
-	--	--	6110[1]	5230[1]	3440[1]	--	--	--	--	--	--	--	--	
-	6480[10]	--	--	2800[9c]	--	--	--	--	--	--	--	--	--	
-	--	--	--	--	--	--	--	50-60[9c]	--	15[9c]	--	--	--	2
-	--	--	--	4090[8]	2004[8]	--	--	--	--	--	--	--	--	
-	--	--	--	--	--	--	--	--	--	--	--	4.33[8]	5.3[8]	2
800[11]	5800[11]	5800[11]	--	--	--	--	--	--	--	--	--	--	--	
.	--	--	--	--	--	59[11]	90[11]	118[11]	54[11]	38[11]	25[11]	--	--	20
.	--	--	--	5990[8]	5743[8]	--	--	--	--	--	--	--	--	
.	--	--	--	--	--	--	--	--	--	--	--	11.7[8]	13.0[8]	2
.	--	--	8550[1]	5480[1]	5200[1]	--	--	--	--	--	--	--	--	
.	6600[12]	--	--	--	--	--	--	--	--	--	--	--	--	
.	--	--	--	--	--	--	71[12]	111[12]	--	11[12]	--	--	--	20
.	--	--	--	5010[8]	3402[8]	--	--	--	--	--	--	--	--	
.	--	--	--	--	--	--	--	--	--	--	--	5.25[8]	4.2[8]	2

Adhesive and Manufacturer	Type	Cure	Adherend	+250°F	+180
5. FM-1000, NO PRIME, Bloomingdale Rubber Co.	Nylon-epoxy	RT-350°F 10°F/min, 1 Hr 350°F 25 psi.	.064" 2024T3 Clad	2600[13]	4320[13]
			.020" " "	--	--
			.064" 2024T3 Bare	--	--
			.064" 7075T6 Bare	--	--
			.020" " "	--	--
			.020" EFH 301 S/S	--	--
6. Resin 3135, Narmco Materials Div., Telecomputing Corp.	Epoxy-polyamide	1/2 Hr 200°F Contact 24 Hr Contact	.064" 2024T3 Clad	--	(200°F) 3000[14]
			.064" 2024T3 Bare	--	--
		"	.064" 7075T6 Bare	--	--
		"	.020" " "	--	--
		"	.020" EFH 301 S/S	--	--
		"	.020" A-110-AT Ti	--	--
7. EC-1933B/A, NO PRIME, Minnesota Mining & Manufacturing Co.	Epoxy-polyamine	2 Hr 150°F Contact	.064" 2024T3 Clad Prime	1100[15]	3500[15]
			.064" 7075T6 Bare	--	--
			.020" " "	--	--
8. Resiweld No. 4, H. B. Fuller Co.	Epoxy-polyamide	24 Hr RT Contact	.064" 2024T3 Bare	--	--
9. EC-1469, Minnesota Mining & Manufacturing Co.	Epoxy	1 Hr 350°F 25 psi.	.064" 2024T3 Clad	--	--
10. Armstrong A-4, Armstrong Products Co.	Epoxy	3/4 Hr 335°F 150 psi.	Na-amide-treated Teflon to SAE 52100 Steel.	--	--
11. Alumina Filled Epoxy	Epoxy	--	Copper	--	--

TABLE I (Continued)

| | Tensile Shear Strength, psi | | | | | | | | | Tee Peel Streng | | | |
Adherend	+250°F	+180	RT	-40	-67	-90	-100	-320	-423	+250°F	+180	RT	-40
.064" 2024T3 Clad	2600_{13}	4320_{13}	7090_{13}	--	7400_{13}	--	--	--	--	--	--	--	--
.020" " "	--	--	--	--	--	--	--	--	--	--	--	60_{13}	--
.064" 2024T3 Bare	--	--	6110_1	--	--	--	5210_1	3790_1	3370_1	--	--	$--_{13}$	--
.064" 7075T6 Bare	--	--	--	--	--	--	--	4310_8	2347_8	--	--	--	--
.020" " "	--	--	--	--	--	--	--	--	--	--	--	--	--
.020" EFH 301 S/S	--	--	3730_1	--	--	--	7450_1	4310_1	3750_1	--	--	--	--
.064" 2024T3 Clad	--	(200°F) 3000_{14}	4500_{14}	--	--	--	--	--	--	--	--	--	--
.064" 2024T3 Bare	--	--	2180_1	--	--	--	1850_1	1760_1	1640_1	--	--	--	--
.064" 7075T6 Bare	--	--	--	--	--	--	--	1514_8	1552_8	--	--	--	--
.020" " "	--	--	--	--	--	--	--	--	--	--	--	--	--
.020" EFH 301 S/S	--	--	1310_1	--	--	--	1830_1	1350_1	940_1	--	--	--	--
.020" A-110-AT Ti	--	--	1040_1	--	--	--	1790_1	1020_1	1020_1	--	--	--	--
.064" 2024T3 Clad Prime	1100_{15}	3500_{15}	4000_{15}	--	3100_{15}	(-85°F) 3400_{15}				--	--	--	--
.064" 7075T6 Bare	--	--	--	--	--	--	--	1775_8	1649_8	--	--	--	--
.020" " "	--	--	--	--	--	--	--	--	--	--	--	--	--
.064" 2024T3 Bare	--	--	2460_1	--	--	--	2380_1	1900_1	2010_1	--	--	--	--
.064" 2024T3 Clad	--	--	2715_3	--	--	--	2715_3	2535_3	2345_3	--	--	--	--
Na-amide-treated Teflon to SAE 52100 Steel.	-- --	-- --	-- --	-- --	-- --	-- --	-- --	6000 8000_4	-- --	-- --	-- --	-- --	-- --
Copper	--	--	3500_5	--	--	--	--	1000_5	1000_5	--	--	--	--

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(Continued)

Shear Strength, psi						Tee Peel Strength, lbs/1"								Peel Rate
.0	-67	-90	-100	-320	-423	+250°F	+180	RT	-40	-67	-90	-320	-423	in/min
	7400_{13}	--	--	--	--	--	--	--	--	--	--	--	--	
	.	--	--	--	--	--	--	60_{13}	--	--	--	--	--	3
	--	--	5210_1	3790_1	3370_1	--	--	--	--	--	--	--	--	
	--	--	--	4310_8	2347_8	--	--	--	--	--	--	--	--	
	--	--	--	--	--	--	--	--	--	--	--	3.1_8	5.5_8	2
	--	--	7450_1	4310_1	3750_1	--	--	--	--	--	--	--	--	
	--	--	--	--	--	--	--	--	--	--	--	--	--	
	--	--	1850_1	1760_1	1640_1	--	--	--	. --	--	--	--	--	
	--	--	--	1514_8	1552_8	--	--	--	--	--	--	--	--	
	--	--	--	--	--	--	--	--	--	--	--	0_8	0_8	2
	--	--	1830_1	1350_1	940_1	--	--	--	--	--	--	--	--	
	--	--	1790_1	1020_1	1020_1	--	--	--	--	--	--	--	--	
	3100_{15}	(-85°F) 3400_{15}				--	--	--	--	--	--	--	--	
	--	--	--	1775_8	1649_8	--	--	--	--	--	--	1.7_8	2.25_8	2
	--	--	2380_1	1900_1	2010_1	--	--	--	--	--	--	--	--	
	--	--	2715_3	2535_3	2345_3	--	--	--	--	--	--	--	--	
	--	--	--	6000	--	--	--	--	--	--	--	--	--	
	--	--	--	8000_4	--	--	--	--	--	--	--	--	--	
	--	--	--	1000_5	1000_5	--	--	--	--	--	--	--	--	

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Adhesive and Manufacturer	Type	Cure	Adherend	+250°F	+180
12. XL967045-B/A, Minnesota Mining & Manufacturing Co.	Epoxy	48 Hr RT Contact	.064" 2024T3 Clad	--	--
13. Metlbond 302, Narmco Materials Div., Telecomputing Corp.	Epoxy-phenolic	1 Hr 350°F 25 psi	.064" 301-1/2H-2B S/S	--	--
			.020" 7075T6 Bare	--	--
			.020" EFH 301 S/S	--	--
			.020" A-110-AT Ti	--	--
14. Epon 422J	Epoxy-phenolic	1 Hr 350°F 25 psi	.064" 301-1/2H-2B S/S	--	--
15. Metlbond 4021, Narmco Materials Div., Telecomputing Corp.	Nitrile Phenolic	1 Hr 350°F 100-200 psi.	.064" 2024T3 Bare	--	2900_2
			.020" " "	--	--
			.064" 2024T3 Clad	--	--
16. Metlbond 4041, Narmco Materials Div., Telecomputing Corp.	Nitrile Phenolic	1 Hr 350°F 100-200 psi.	.064" 2024T3 Bare	--	2500_2
			.020" " "	--	--
			.020" EFH 301 S/S	--	--
			.020" A-110-AT Ti	--	--
17. AF-32, Minnesota Mining & Manufacturing Co.	Nitrile Phenolic	1 Hr 350°F 100 psi.	.020" EFH 301 S/S	--	--
18. AF-13, Minnesota Mining & Manufacturing Co.	Nitrile Phenolic	1/2 Hr 350°F 120 psi	Na-amide-treated Teflon to SAF 52100 Steel	--	--
				--	--
19. AF-5930, Minnesota Mining & Manufacturing Co.	Nitrile Phenolic	1 Hr 350°F 150 psi	.064" 2024T3 Clad	--	--
20. Bondmaster M24B, Rubber & Asbestos Corp.	Rubber-epoxy-phenolic	1 Hr 350°F 50 psi	.064" 2024T3 Clad	--	--

TABLE I (Continued)

| Adherend | Tensile Shear Strength, psi | | | | | | | | | Tee Peel Stren | | | |
	+250°F	+180	RT	-40	-67	-90	-100	-320	-423	+250	+180	RT	-40
.064" 2024T3 Clad	--	--	2390_{16}	--	--	--	2200_{16}	--	--	--	--	--	--
.064" 301-1/2H-2B S/S	--	--	2595_3	--	--	--	2585_3	3135_3	3000_3	--	--	--	--
.020" 7075T6 Bare	--	--	--	--	--	--	--	--	--	--	--	3.33_8	--
.020" EFH 301 S/S	--	--	2490_1	--	--	--	2780_1	2800_1	2690_1	--	--	--	--
.020" A-110-AT Ti	--	--	800_1	--	--	--	1440_1	1920_1	1560_1	--	--	--	--
.064" 301-1/2H-2B S/S	--	--	3315_3	--	--	--	3650_3	3145_3	3240_3	--	--	--	--
.064" 2024T3 Bare	--	2900_2	3750_2	--	3400_2	--	--	--	--	--	--	--	--
.020" " "	--	--	--	--	--	--	--	--	--	--	--	45_2	5.
.064" 2024T3 Clad	--	--	4295_3	--	--	--	4125_3	1620_3	1085_3	--	--	--	--
.064" 2024T3 Bare	--	2500_2	3750_2	--	6200_2	--	5020_1	4400_1	1710_1	--	--	--	--
.020" " "	--	--	--	--	--	--	--	--	--	--	12_2	22_2	32.
.020" EFH 301 S/S	--	--	2580_1	--	--	--	8700_1	5810_1	2070_1	--	--	--	--
.020" A-110-AT Ti	--	--	1590_1	--	--	--	6220_1	3690_1	1420_1	--	--	--	--
.020" EFH 301 S/S	--	--	3650_1	--	--	--	8490_1	3600_1	2750_1	--	--	--	--
Na-amide-treated Teflon to SAE 52100 Steel	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	-- / --	6250 / 7000_4	-- / --	-- / --	-- / --	-- / --	-- / --
.064" 2024T3 Clad	--	--	3920_3	--	--	--	3795_3	1225_3	--	--	--	--	--
.064" 2024T3 Clad	--	--	3625_3	--	--	--	1635_3	1230_3	1045_3	--	--	--	--

(Continued)

e Shear Strength, psi						Tee Peel Strength, lbs/1"								Peel Rate in/min
40	-67	-90	-100	-320	-423	+250	+180	RT	-40	-67	-90	-320	-423	
--	--	--	2200_{16}	--	--	--	--	--	--	--	--	--	--	
--	--	--	2585_3	3135_3	3000_3	--	--	--	--	--	--	--	--	
--	--	--	--	--	--	--	--	3.33_8	--	--	--	3.66_8	--	2
--	--	--	2780_1	2800_1	2690_1	--	--	--	--	--	--	--	--	
--	--	--	1440_1	1920_1	1560_1	--	--	--	--	--	--	--	--	
--	--	--	3650_3	3145_3	3240_3	--	--	--	--	--	--	--	--	
--	3400_2	--	--	--	--	--	--	--	--	--	--	--	--	
--	--	--	--	--	--	--	--	45_2	5.0_2	5.0_2	--	--	--	2
--	--	--	4125_3	1620_3	1085_3	--	--	--	--	--	--	--	--	
--	6200_2	--	5020_1	4400_1	1710_1	--	--	--	--	--	--	--	--	
--	--	--	--	--	--	--	12_2	22_2	32_2	14_2	--	--	--	2
--	--	--	8700_1	5810_1	2070_1	--	--	--	--	--	--	--	--	
--	--	--	6220_1	3690_1	1420_1	--	--	--	--	--	--	--	--	
--	--	--	8490_1	3600_1	2750_1	--	--	--	--	--	--	--	--	
--	--	--	--	6250	--	--	--	--	--	--	--	--	--	
--	--	--	--	7000_4	--	--	--	--	--	--	--	--	--	
--	--	--	3795_3	1225_3	--	--	--	--	--	--	--	--	--	
--	--	--	1635_3	1230_3	1045_3	--	--	--	--	--	--	--	--	

Adhesive and Manufacturer	Type	Cure	Adherend	+250°F	+180
21. Plastilock 601, B. F. Goodrich Co.	Rubber Resin	Mfg. Recommended	.064" 2024T3 Bare .020" " "	-- --	2000 --
22. Bondmaster 648, Rubber & Asbestos Corp.	Rubber Resin	3/4 Hr 330°F 150 psi	Na-amide-treated Teflon to SAE 52100 Steel	--	--
23. Scotchweld 583, Minnesota Mining & Manufacturing Co.	Rubber Resin	3/4 Hr 330°F 150 psi	Na-amide-treated Teflon to SAE 52100 Steel	--	--
24. Bondmaster 653, Rubber & Asbestos Corp.	Rubber Resin	3/4 Hr 330°F 150 psi	Na-amide-treated Teflon to SAE 52100 Steel	--	--
25. Metlbond 303(MN3C), Narmco Materials Div., Telecomputing Corp.	Neoprene Nylon Phenolic	3/4 Hr 330°F 40 psi 3/4 Hr 330°F 150 psi	.064" 2024T3 Clad Na-amide-treated Teflon to SAE 52100 Steel	-- --	1620 --
26. Narmtape 111, Narmco Materials Div., Telecomputing Corp.	Nylon Phenolic Epoxy	1 Hr 350°F 25 psi	.064" 2024T3 Bare .020" " "	-- --	2750 --
27. APCO-1261, Applied Plastics Div., Hexcel Products Co.	Poly-urethane	1/2 Hr 300°F Contact under 100 psi nitrogen.	.064" 7075T6 Bare .020" " "	-- --	-- --
28. APCO-1219, Applied Plastics Div., Hexcel Products Co.	Poly-urethane	24 Hr RT Contact	.064" 2024T3 Bare .020" EFH 301 S/S	-- --	-- --
29. Swedlow 371W, Swedlow Plastics Co.	Vinyl Phenolic	1/2 Hr 340°F 5 psi	.064" 2024T3 Clad	--	--
30. FM-47, Bloomingdale Rubber Co.	Vinyl Phenolic	1 Hr 350°F 200 psi	.064" 2024T3 Clad	--	--
31. Redux 775, Ciba Co., Inc.	Vinyl Phenolic	1/2 Hr 340°F 100 psi	.064" 2024T3 Clad	--	--
32. EC-1471, Minnesota Mining & Manufacturing Co.	Vinyl Phenolic	1 Hr 350°F 150 psi	.064" 2024T3 Clad	--	--

NOTE: The subscripts in Table I refer to the references below.

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3. Frost, William M., "Strength of Structural Adhesives at Temperatures Down to Minus 424°F," WADC Technical Report 59-260, November 1959.

4. Eppinger, C. E. and Love, W. J., "Bonding Plastic to Metal for High Strength at Low Temperature," Advances in Cryogenic Engineering, Vol. 4, page 123.

5. McClintock, R. M. and Hiza, M. J., "Epoxy Resins as Cryogenic Structural Adhesives," CEL, NBS, Boulder, Colo., also Modern Plastics, 35, 172 (1958); also NBS Report 5093 (1957). "Low Temperature Strength of Epoxy Resin Adhesives," NBS Technical News Bulletin, Vol. 24, No. 5, page 84 (1958).

6. "Adhesive Properties Minus 300°F to Plus 700°F," North American Aviation, AF 33(600)-28469, ASTIA 151529, September 1957.

7. "Qualification No. 01027, Narm Corp., June 196

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9. Smith, M. Bruce Sandwich Adhesi Research & Deve
   a. Progre
   b. Narmco
   c. Final

10. "Qualification Test Report No Telecomputing

11. "AF-40," Aircr Manufacturing

TABLE I   (Continued)

| Adherend | Tensile Shear Strength, psi | | | | | | | | | Tee Peel Strength, | | | |
	+250°F	+180	RT	-40	-67	-90	-100	-320	-423	+250	+180	RT	-40
.064" 2024T3 Bare	--	2000_2	3750_2	1250_2	1250_2	--	--	--	--	--	--	--	--
.020" " "	--	--	--	--	--	--	--	--	--	--	17_2	18_2	1.0_2
Na-amide-treated Teflon to SAE 52100 Steel	--	--	--	--	--	--	--	3000 3750_4	--	--	--	--	--
Na-amide-treated Teflon to SAE 52100 Steel	--	--	--	--	--	--	--	3500 4500_4	--	--	--	--	--
Na-amide-treated Teflon to SAE 52100 Steel	--	--	--	--	--	--	--	5500 7500_4	--	--	--	--	--
.064" 2024T3 Clad	--	1620_{17}	2930_{17}	--	5430_{17}	--	--	--	--	--	--	--	--
Na-amide-treated Teflon to SAE 52100 Steel	--	--	--	--	--	--	--	3750_4	--	--	--	--	--
.064" 2024T3 Bare	--	2750_2	3500_2	1500_2	1500_2	--	--	--	--	--	--	--	--
.020" " "	--	--	--	--	--	--	--	--	--	--	45_2	22_2	3_2
.064" 7075T6 Bare	--	--	1332_8	--	--	--	--	1940_8	--	--	--	--	--
.020" " "	--	--	--	--	--	--	--	--	--	--	--	1.92_8	--
.064" 2024T3 Bare	--	--	1310_1	--	--	--	3100_1	2980_1	2710_1	--	--	--	--
.020" EFH 301 S/S	--	--	840_1	--	--	--	2210_1	1640_1	1020_1	--	--	--	--
.064" 2024T3 Clad	--	--	4855_3	--	--	--	2450_3	1795_3	1395_3	--	--	--	--
.064" 2024T3 Clad	--	--	4600_3	--	--	--	3040_3	2325_3	1915_3	--	--	--	--
.064" 2024T3 Clad	--	--	3995_3	--	--	--	3200_3	2035_3	--	--	--	--	--
.064" 2024T3 Clad	--	--	5725_3	--	--	--	3455_3	2070_3	--	--	--	--	--

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Vol. 24,

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7. "Qualification of Metlbond 406 to Type I, MIL-A-5090D," Test Report No. 01027, Narmco Research & Development, a Division of Telecomputing Corp., June 1960.

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   b. Narmco Brochure ADS. 12.
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12. "AF-41," Aircraft Produc Manufacturing Co.

13. "FM-1000 Adhesive Film,"

14. "Narmco Formula 3135 Res Telecomputing Corp.

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(Continued)

Shear Strength, psi						Tee Peel Strength, lbs/1"								Peel Rate
-40	-67	-90	-100	-320	-423	+250	+180	RT	-40	-67	-90	-320	-423	in/min
250_2	1250_2	--	--	--	--	--	--	--	--	--	--	--	--	
--	--	--	--	--	--	--	17_2	18_2	1.0_2	1.0_2	--	--	--	2
--	--	--	--	3000 3750_4	--	--	--	--	--	--	--	--	--	
--	--	--	--	3500 4500_4	--	--	--	--	--	--	--	--	--	
--	--	--	--	5500 7500_4	--	--	--	--	--	--	--	--	--	
--	5430_{17}	--	--	--	--	--	--	--	--	--	--	--	--	
--	--	--	--	3750_4	--	--	--	--	--	--	--	--	--	
500_2	1500_2	--	--	--	--	--	--	--	--	--	--	--	--	
--	--	--	--	--	--	--	45_2	22_2	3_2	3_2	--	--	--	2
--	--	--	--	1940_8	--	--	--	--	--	--	--	--	--	
--	--	--	--	--	--	--	--	1.92_8	--	--	--	3.33_8	--	2
--	--	--	3100_1	2980_1	2710_1	--	--	--	--	--	--	--	--	
--	--	--	2210_1	1640_1	1020_1	--	--	--	--	--	--	--	--	
--	--	--	2450_3	1795_3	1395_3	--	--	--	--	--	--	--	--	
--	--	--	3040_3	2325_3	1915_3	--	--	--	--	--	--	--	--	
--	--	--	3200_3	2035_3	--	--	--	--	--	--	--	--	--	
--	--	--	3455_3	2070_3	--	--	--	--	--	--	--	--	--	

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15. "3M Adhesive EC-1933B/A," Issue #1, Minnesota Mining & Manufacturing Co.

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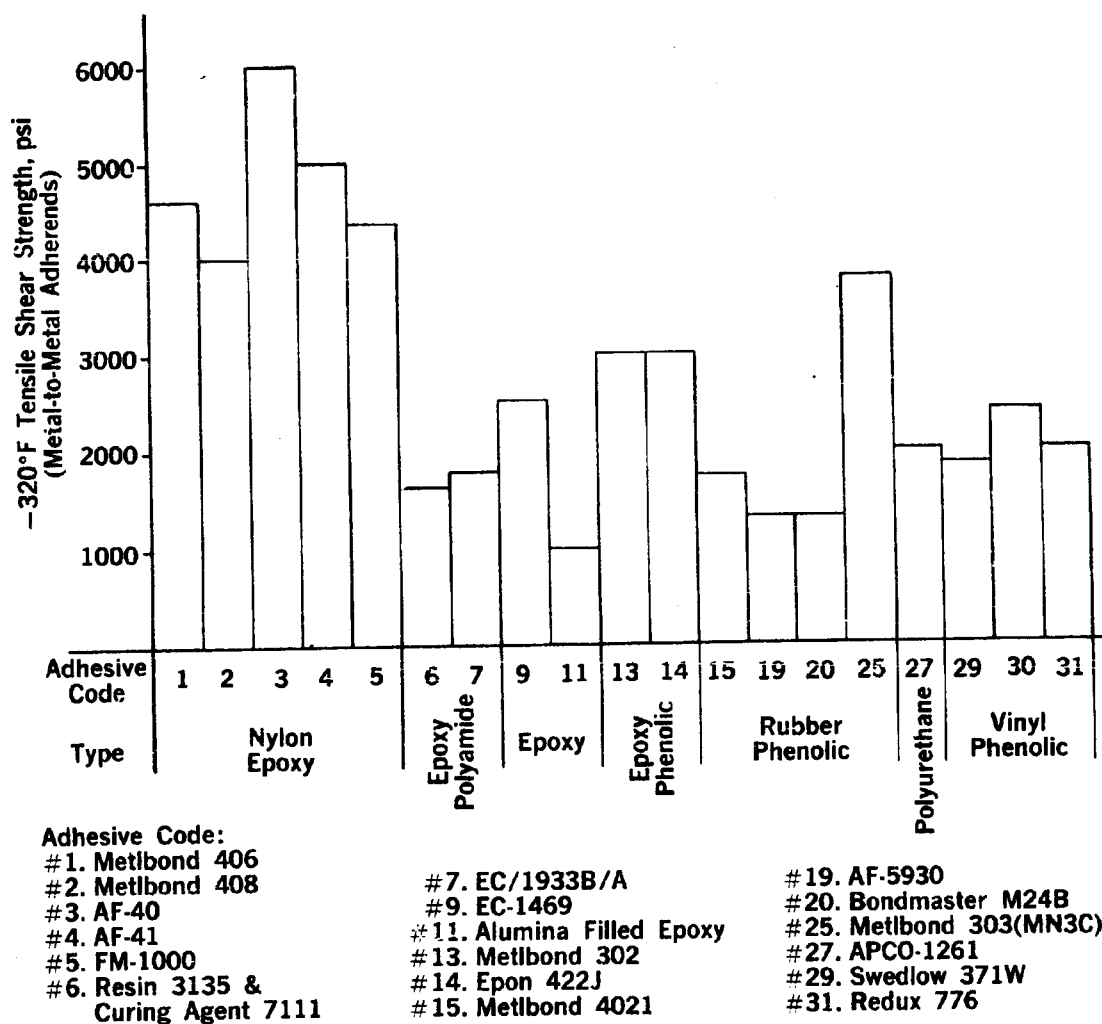
Figure 1. Basis for Selection of Existing Adhesive Types.

Adhesive Code:
#1. Metlbond 406
#2. Metlbond 408
#3. AF-40
#4. AF-41
#5. FM-1000
#6. Resin 3135 &
    Curing Agent 7111

#7. EC/1933B/A
#9. EC-1469
#11. Alumina Filled Epoxy
#13. Metlbond 302
#14. Epon 422J
#15. Metlbond 4021

#19. AF-5930
#20. Bondmaster M24B
#25. Metlbond 303(MN3C)
#27. APCO-1261
#29. Swedlow 371W
#31. Redux 776

IV. EXISTING ADHESIVE EVALUATION

In establishing the performance characteristics of the best available materials mentioned above, a testing program was established. In addition to the general requirements listed in the Introduction, it is belived that tensile shear strength and tee peel strength are outstanding qualifying tests for adhesives. It is firmly belived that the tensile shear test defines the strength of an adhesive, and that the tee peel test defines the toughness or flexibility of the adhesive.

The following step-wise screening procedure was established to evaluate adhesives — both existing and newly developed systems:

Step 1. Tensile shear and tee peel strength at -320 and +75°F.

Step 2. Tensile shear and tee peel strength over temperature range from -423 to +260°F.

Step 3. The most promising members of each category of adhesives should then be tested in the following parameters:

      a. Mechanical shock
      b. Butt tensile
      c. Compression
      d. LOX compatibility

When development work was begun, the new adhesives were progressively tested until they failed to meet values established by testing of the best commercially available materials.

A. Tensile Shear

The alloy selected for evaluation was .064" 7075T6 bare aluminum. Die-cut break away type panels, yielding eight 1" wide specimens, (see Figure 2) were selected instead of MIL-A-5090D solid panels so that little or no damage would result from separation of the panels into 1" wide test specimens. Surface preparation consisted of a methyl ethyl ketone degrease, standard FPL sodium dichromate-sulfuric acid etch,* distilled water rinse, and 150°F oven dry. This design and surface treatment was used throughout the program, except where it is otherwise noted.

The non-rolled, square, deburred and sharp sides of the die-cut break away panels were selected as the faying surfaces. A strip of adhesive measuring approximately 1" x 10 1/4" was interposed between the faying surfaces and the bond, and assembled with 1/2" overlap, using a curing fixture made from 1/2" square steel bar stock equipped with pins to assure alignment of the 1" edges of each specimen. No prime was employed. Paste adhesives were applied to the faying surfaces with a spatula, and .004" soft aluminum wire was layed in the glueline to control thickness.

---

*Immersed 5-10 minutes in a solution maintained at 150-160°F of 30 parts by weight sodium dichromate, 170 parts by weight distilled water, and 50 parts by weight concentrated sulfuric acid.

9 3/4"

4"

.064" ± .001"
7075T6 Bare
Aluminum Alloy

½" overlap

1/2"

1/4" Retain
Tabs

8-3/8"
Holes

1.000
± .005

½"

Bonded
Reinforcing
Strips

Die cut tensile shear panels
bonded with half-inch overlap
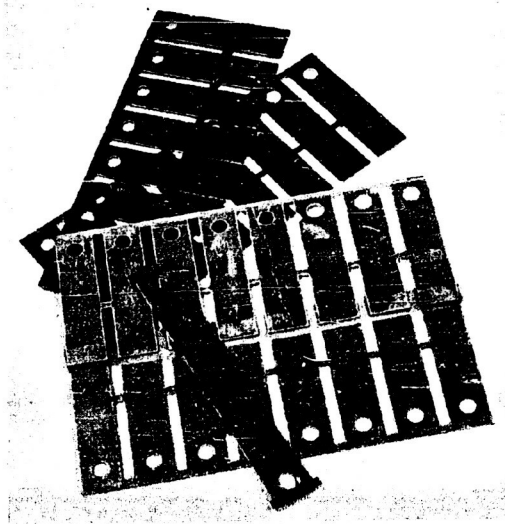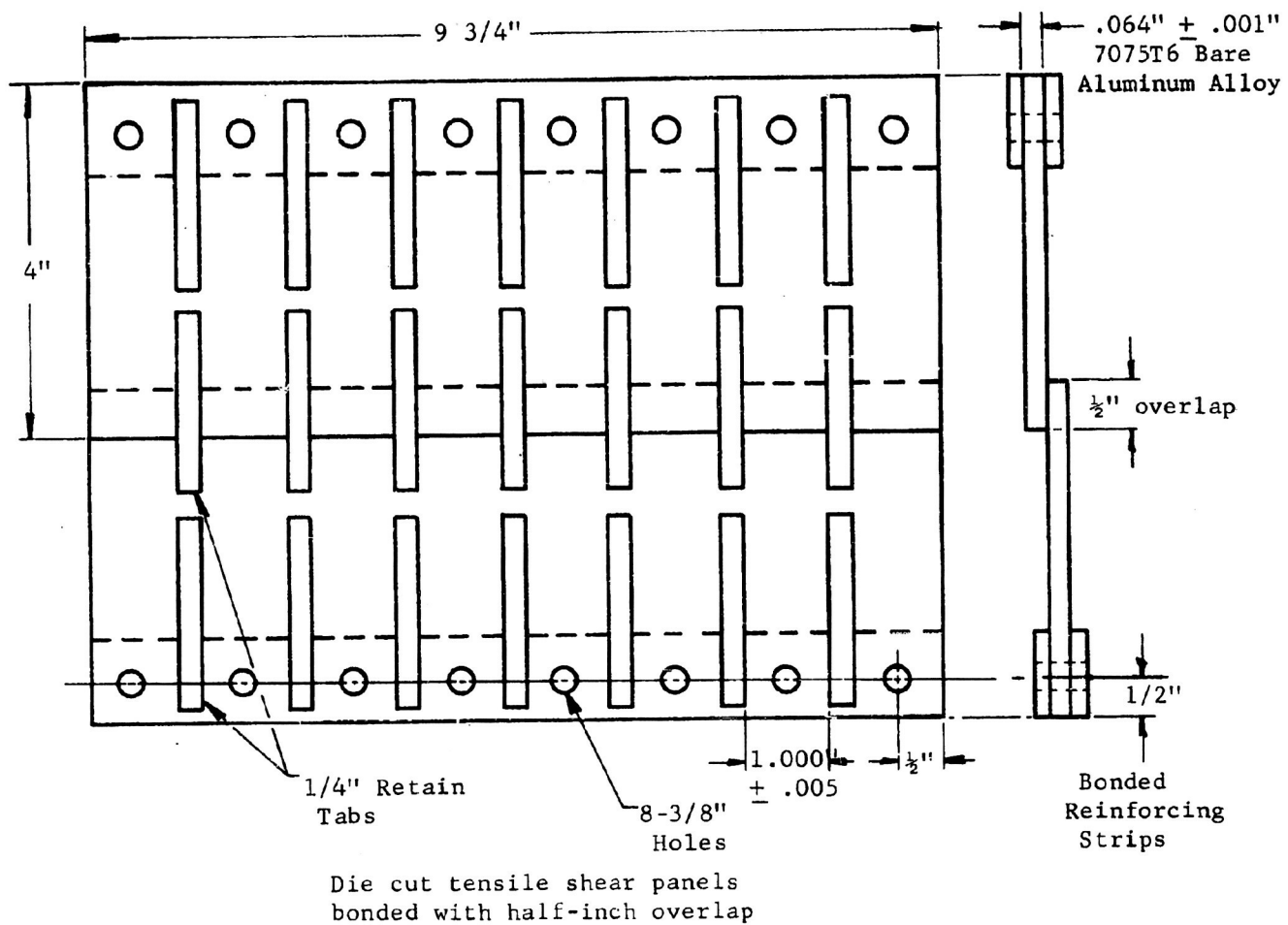
Figure 2.   Specimen design for tensile shear tests.

The bond assembly was press cured according to the manufacturer's recommended time, temperature, and pressure cycle. A thermocouple located immediately adjacent to the overlap area was employed for monitoring temperature. Room temperature cures were accomplished by dead-loading the fixtures to assure contact pressure.

Special procedures were employed for bonding with APCO-1261 polyurethane, because this material is not suggested as a metal-to-metal adhesive, and because the prepolymer is in solvent solution and also hygroscopic. The manufacturer's suggestions were followed for mixing the prepolymers. The mixture was applied to the faying surfaces of the test specimens by brush coating. The coated panels were immediately placed in a vacuum desiccator and dried for about 1 hour at 15" Hg. Panels were then removed from the desiccator, assembled with 1/2" overlap in the curing fixture, and placed in an autoclave where 100 psi inert atmosphere (nitrogen) was applied and curing accomplished. The resulting bonds were void-free.

Other than following manufacturer's recommendations, no other means were taken to optimize the bonds. Bonding conditions for existing adhesives are listed in Table 1 under heading, "Cure."

Because of the very high load required to fail the nylon-epoxy bonds, it was necessary to reinforce the gripped ends of the specimens. This was done by bonding a .064" 7075T6 bare aluminum doubler, 1" by 9-3/4", to each side of the ends of the specimen surrounding the 3/8" pin grip holes with Metlbond 406, (see Figure 2). This, of course, necessitated spotting the holes through the bonded area as well as sawing through the reinforcement. All other adhesive specimens were prepared without reinforcement.

Testing in tensile shear at -320°F was accomplished on a 20,000-pound capacity Tinius Olsen testing machine. (See Figure 3.) The specimens were loaded with pin grips. A cryostat was built around the lower grip and was designed to slide up and down the machine loading rod to allow easy access to the specimen. The test specimens were accordingly positioned in the machine, and located with pins. The cryostat containing liquid nitrogen was then moved up so that the bonded area was completely immersed in the cryogenic fluid. After approximately 10 minutes, the liquid nitrogen ceased boiling, and the specimen was loaded in accordance with MIL-A-5090D. The failing load was recorded and used to calculate tensile shear strength.

Tensile shear testing at liquid hydrogen temperature was performed on a 10,000-pound Instron testing machine, shown in Figures 4, 5, and 6. Hydrogen storage is shown in Figure 7. Loading was in accordance with MIL-A-5090D, and the loading was automatically recorded.

Table 2 gives a comprehensive analysis of the -320 and -423°F tensile shear strength of the selected existing commercial adhesives. The spread in values undoubtedly results from non-optimized bonding and curing conditions, glueline thickness, etc.

It was concluded that the low temperature tensile shear strengths compared favorably with existing data, and pointed to the superiority of the nylon-epoxy adhesives at extremely low temperature.

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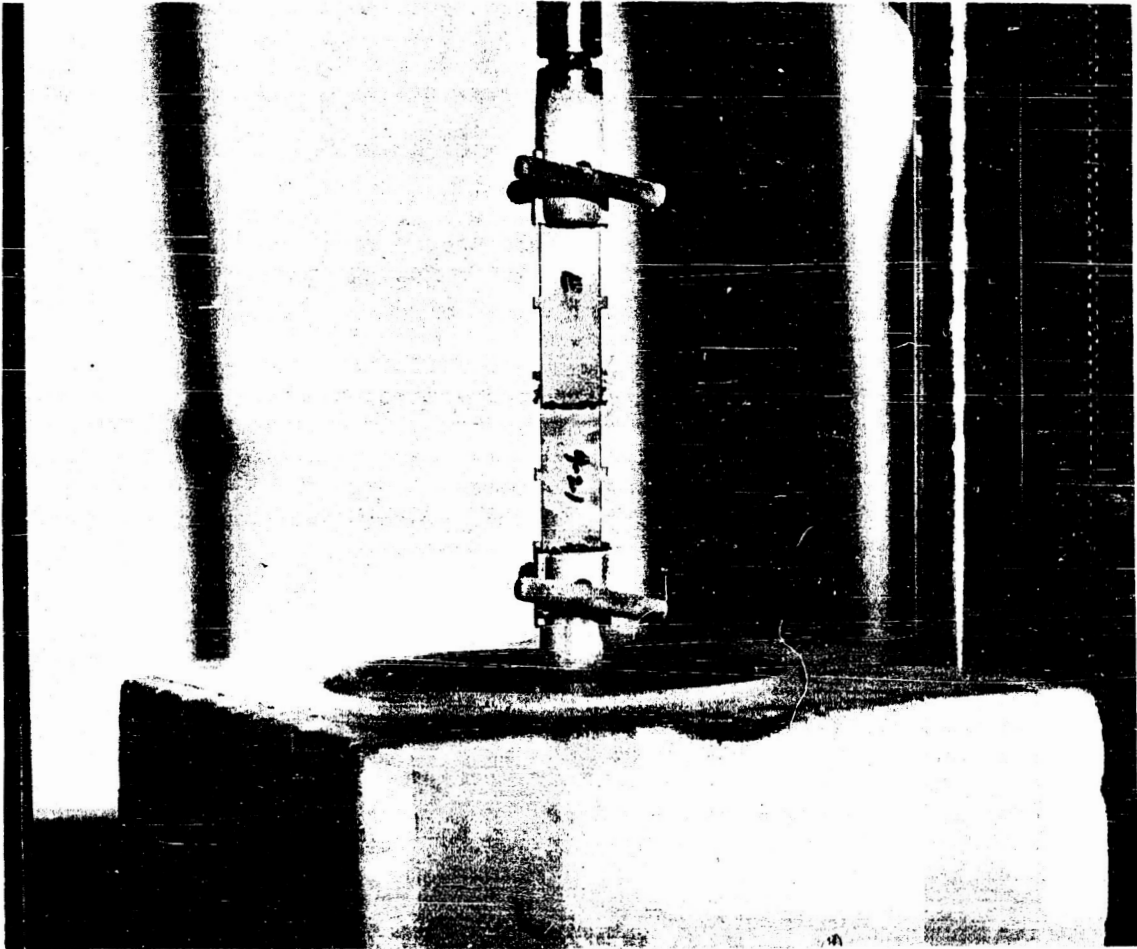
Figure 3.   Tensile shear specimen about to be tested in liquid
nitrogen.   The cryostat will be raised to immerse
the specimen, followed by testing to failure.

Figure 4. Tensile shear and tee
peel tests at -423°F are performed
on the Instron testing machine in
foreground. Shown are cryostat in
position, liquid hydrogen level
control, liquid hydrogen dewar, and
delivery line.
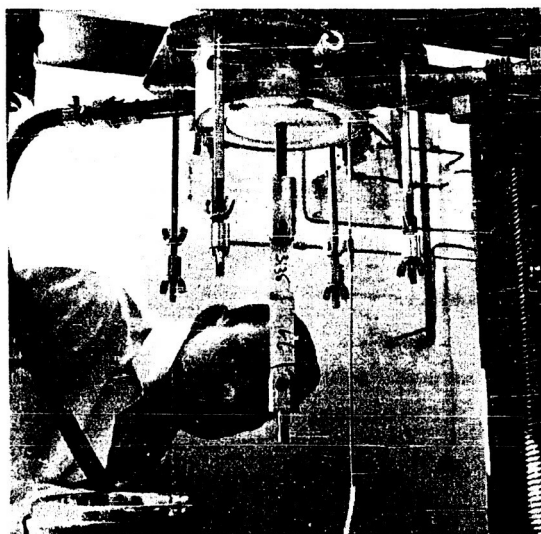
Figure 5. Cryostat removed from its
mounts on Instron testing machine,
showing half-inch overlap bonded
specimen in partial position for
tensile shear testing at -423°F.
Liquid level probe is immediately
to right of specimen, hydrogen
delivery line is at right, and
purge line at left.

Figure 6. Console for the Instron
testing machine is separated by
partition as a safety precaution.
Operator conducts the test by
viewing machine through a safety
window.
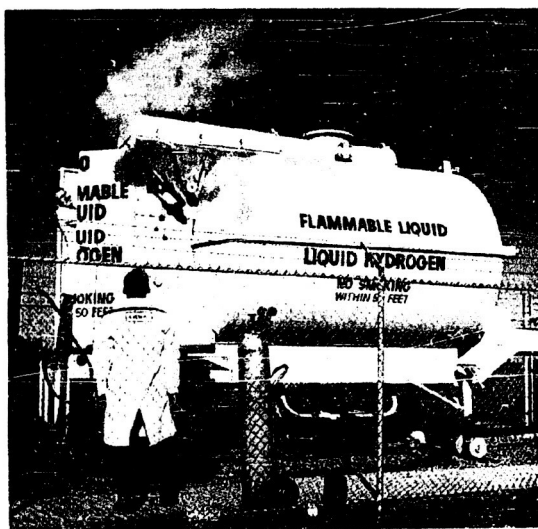
Figure 7. Outdoor bulk storage of
liquid hydrogen in a trailer,
showing manual venting of gaseous
hydrogen. Liquid hydrogen is
transferred to the 200-liter mobile
dewar shown in Figure 4 for use in
the laboratory.

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TABLE 2

EXISTING ADHESIVE EVALUATION

-320 and -423°F Tensile Shear Strength

Adhesive and Manufacturer*	Type	Glueline Thickness, inches	Test Temperature, °F	Tensile Shear, psi	Failure	
					% Adhesion	% Cohesion
Metlbond 406, NO PRIME, Narmco Materials Div., Tele- computing Corp.	Nylon- epoxy	.002 .002 .003 .003 .003 .003 .002 .002	-320	5650 4490 4350 3670 4270 5060 5400 5830 Avg. 4840	100 100 100 100 100 100 100 100	- - - - - - - -
"	"	.003 .003 .003 .002 .002 .002	-423	3580 3744 3640 3720 3996 4200 Avg. 3813	100 100 100 100 100 100	- - - - - -
Metlbond 408, NO PRIME, Narmco Materials Div., Tele- computing Corp.	Nylon- epoxy	.001 .001 .001 .001 .001 .001 .001 .001	-320	2970 4060 4200 3850 4200 4630 4400 4380 Avg. 4090	100 100 100 100 100 100 100 100	- - - - - - - -
"	"	.0015 .001 .001 .001 .001 .001 .001 .001	-423	1890 2460 2076 1348 Data not Collected 1606 2910 1740 Avg. 2004	100 100 100 100 100 100 100 100	- - - - - - - -

(Continued on next page)

* Bonds were cured according to manufacturer's recommendations with no attempt to optimize. No prime was used.

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TABLE 2 (Continued)

Adhesive and Manufacturer*	Type	Glueline Thickness, inches	Test Temperature, °F	Tensile Shear, psi	Failure	
					% Adhesion	% Cohesion
AF-40, NO PRIME, Minnesota Mining & Manufacturing Co.		.006	-320	6200	100	--
		.008		5870	100	--
		.008		6100	100	--
		.008		6310	100	--
		.008		5900	100	--
		.008		5670	100	--
		.007		6150	100	--
		.006		5750	100	--
				Avg. 5990		
AF-40, NO PRIME Minnesota Mining & Manufacturing Co.	Nylon-epoxy	.005	-423	5740	100	--
		.006		5900	100	--
		.006		5580	100	--
		.006		5100	100	--
		.006		6220	100	--
		.007		5280	100	--
		.007		6220	100	--
		.006		5910	100	--
				Avg. 5743		
AF-41, NO PRIME Minnesota Mining & Manufacturing Co.	Nylon-epoxy	.001	-320	4430	100	--
		.001		4610	100	--
		.001		6020	100	--
		.001		4930	100	--
		.001		4880	100	--
		.001		5260	100	--
		.001		5120	100	--
		.001		4810	100	--
				Avg. 5010		
"	"	.002	-423	3880	100	--
		.002		3180	100	--
		.003		3060	100	--
		.002		3740	100	--
		.001		3480	100	--
		.002		3520	100	--
		.002		3540	100	--
		.003		2820	100	--
				Avg. 3402		

* Bonds were cured according to manufacturer's recommendations with no attempt to optimize. No prime was used.

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TABLE 2 (Continued)

Adhesive and Manufacture*	Type	Glueline Thickness, inches	Test Temperature, °F	Tensile Shear, psi	Failure	
					% Adhesion	% Cohesion
FM-100, NO PRIME Bloomingdale Rubber Co.		.001	-320	4950	90	10
		.001		3260	95	5
		.001		6490	90	10
		.001		3850	85	15
		.001		3840	80	20
		.001		5040	90	10
		.001		2980	90	10
		.001		4070	90	10
				Avg. 4310		
"	"	.002	-423	1920	100	--
		.001		2780	100	--
		.001		2340	100	--
		.001		2640	100	--
		.001		2260	100	--
		.002		1900	100	--
		.001		2680	100	--
		.002		2260	100	00
				Avg. 2347		
Resin 3135, Narmco Materials Div., Tele-computing Corp.	Epoxy-poly-amide	.003	-320	1660	100	--
		.003		1580	100	--
		.003		1510	100	--
		.003		1400	100	--
		.004		1350	100	--
		.003		1544	100	--
		.003		1560	100	--
		.003		1514	100	--
				Avg. 1514		
"	"	.003	-423	1260	100	--
		.003		1640	100	--
		.003		1580	100	--
		.003		1622	100	--
		.004		1590	100	--
		.003		1624	100	--
				Avg. 1552		

(Continued on next page)

* Bonds were cured according to manufacturer's recommendations with no attempt to optimize. No prime was used.

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TABLE 2 (Continued)

Adhesive and Manufacturer*	Type	Glueline Thickness, inches	Test Temperature, °F	Tensile Shear, psi	Failure	
					% Adhesion	% Cohesion
EC-1933B/A, Minnesota Mining & Manufacturing Co.	Filled Epoxy poly-amide	.004 .004 .004 .004 .004 .004 .004 .004	-320	2040 1640 1640 1740 1640 2050 1700 1750 Avg. 1775	100 100 100 100 100 100 100 100	-- -- -- -- -- -- -- --
"	"	.0035 .003 .0035 .003 .0025 .0025	-423	1680 1586 1536 1640 1716 1736 Avg. 1649	100 100 100 100 100 100	-- -- -- -- -- --
APCO-1261, Applied Plastics Div., Hexcell Products Co.	Poly-ure-thane	.004 .004 .005 .005 .003 .004 .004 .005	-320	2190 1890 1980 1910 2400 2350 1560 1310 Avg. 1940	40 40 50 50 60 90 80 50	60 60 50 50 40 10 20 50

* Bonds were cured according to manufacturer's recommendations with attempt to optimize. No prime was used.

B.   Tee Peel

The alloy selected for evaluation was .020" 7075T6 bare aluminum. Stock for bonding was cut 1" ± .01" wide and 12" long. Figure 8 illustrates the specimen with 3/8" holes for grips. The same surface preparation used for the tensile shear specimens was used. The nonrolled, square, deburred, and sharp sides of these strips were selected as the faying surfaces. A strip of adhesive approximately 1-1/2" wide and 11-1/2" long was interposed between the faying surfaces, and the bond was assembled with total overlap (except for 1" unbonded length at grips), using a curing fixture made from 1/2" aluminum plates with aligning pins for the 1" edges and cavities for 6 individual specimens. Alpha cellulose paper was used under and over each specimen to equalize pressure. No prime was employed. Liquid or paste adhesives were applied to faying surfaces with a spatula, and .004" soft aluminum wire was layed in the glueline to control thickness. This design was used throughout the program, except where it is otherwise noted.

The bond assembly was press cured in the same manner as the tensile shear specimens. The special procedures for bonding with APCO-1261 were again employed. At this point the curing fixture was replaced by an autoclave to supply the required inert atmosphere.

The only method employed to optimize tee peel bonds was the method suggested by the manufacturer's recommendations. Bonding procedures are listed in Table 1 under the heading, "Cure." Room temperature cures were accomplished by dead-loading the fixtures to assure contact pressure.

Reinforcement of the gripping ends of the specimens was not necessary. Testing in tee peel at -320°F was accomplished on the same machine and with the same cryostat used for tensile shear (see Figure 9). The specimens were cut in lengths to suit the cryostat and to keep the specimen immersed in the cryogenic media. This left about 2-1/2 bonded length for peeling, or about 4" machine head travel. The specimen was loaded at a head travel of 2" per minute, causing a specimen separation of 1" per minute. An automatic autograph of the load was made during the test, with the average load expressed as pounds of tee peel per inch of width.

Table 3 gives a comprehensive analysis of results of the -320 and -423°F tee peel strength of the selected existing commercial adhesives. Again, the spread in values is probably the result of nonoptimized conditions of cure, glueline thickness, etc. To our knowledge, this is the first reported tee peel data at extremely low temperature, at least for the specific adhesives tested. Again, the superiority of the nylon-epoxy adhesives is emphasized.

C.   Mechanical Shock

The alloy selected for mechanical shock testing was also 7075T6 bare aluminum alloy. The specimen configuration is shown in Figure 10. A special fixture was built for positioning Part A and Part B of the specimen during the adhesive bonding operation. The total bonded area of a combined set of specimens was 0.500 square inch. Surface preparation prior to bonding was the standard sodium dichromate sulfuric acid etch. Curing was accomplished under conditions identical to tensile shear and tee peel specimen preparation.

5" for RT tests,
3" for -320°F,
2" for -423°F

Bend on ¼" R

Cut off
to required
length

Approx. 1"

3/8" Hole

1.00" ± .01"

½"

½"

Bonded Tee Peel Specimen .020" ± .001"
7075T6 Aluminum Alloy
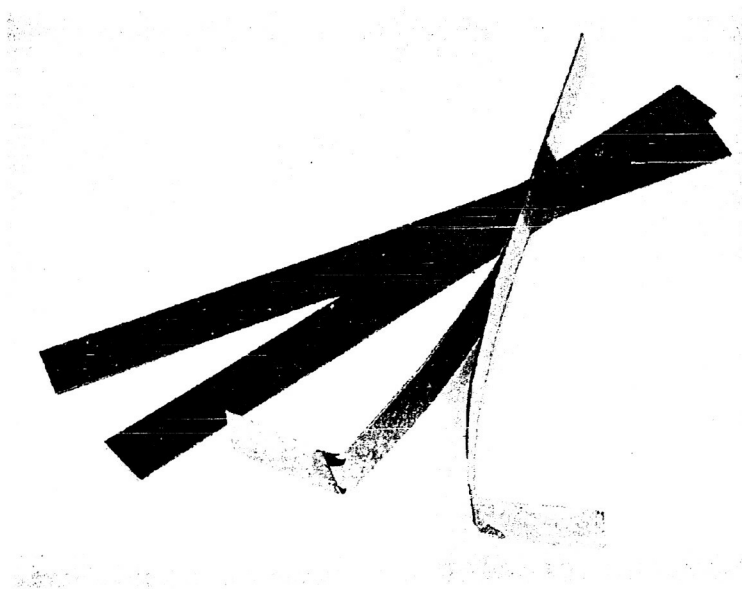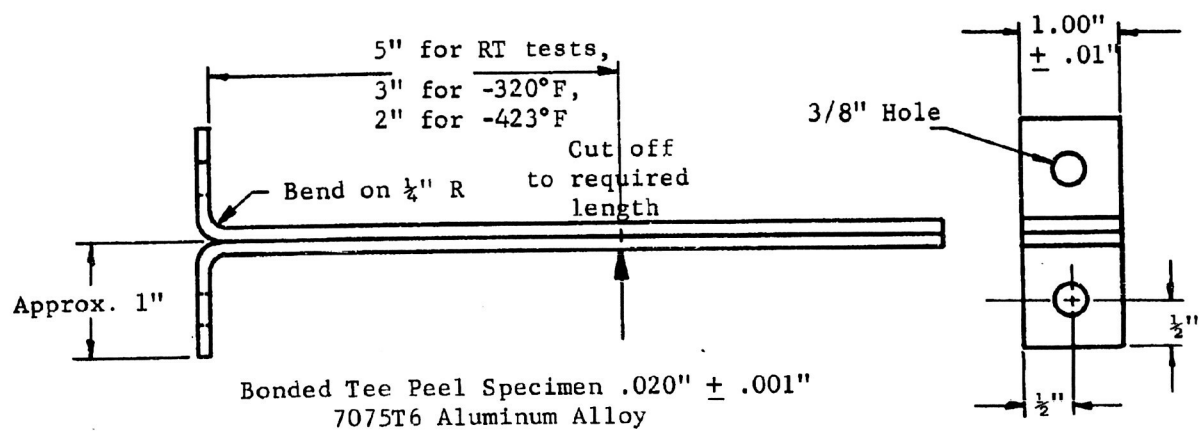
Figure 8. Specimen design for tee peel tests.

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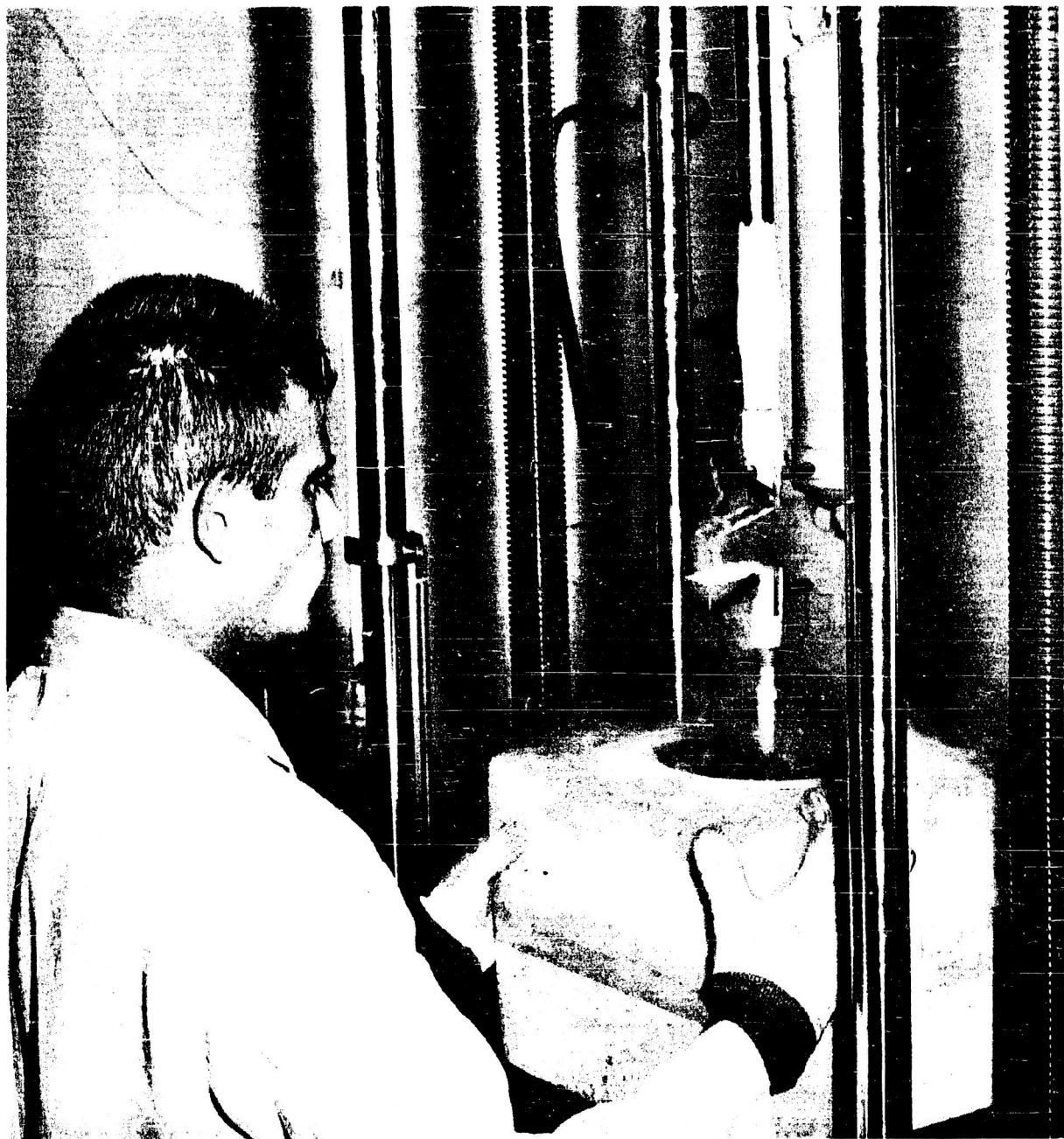
Figure 9. A tee peel specimen has just been failed at liquid nitrogen temperature and the cryostat is being lowered to allow specimen removal and replacement.

TABLE 3

EXISTING ADHESIVE EVALUATION

-320 and -423°F Tee Peel Strength

Adhesive and Manufacturer*	Type	Glueline Thickness, inches	Test Temperature, °F	Tee Peel, lbs/1"	Failure % Adhesion	Failure % Cohesion
Metlbond 406, NO PRIME, Narmco Materials Div., Tele-computing Corp.	Nylon-epoxy	.004 .004 .004 .004 .004 .004	-320	8.0 11.5 8.0 7.5 9.0 6.0 Avg. 8.33	-- -- -- -- -- --	100 100 100 100 100 100
"	"	.004 .004 .004	-423	9.0 9.0 6.5 Avg. 8.2	-- -- --	100 100 100
Metlbond 408, NO PRIME, Narmco Materials Div., Tele-computing Corp.	Nylon-epoxy	.003 .005 .005 .005 .004 .004	-320	4.0 4.0 4.0 4.0 4.0 6.0 Avg. 4.33	40 40 40 40 40 40	60 60 60 60 60 60
"	"	.005	-423	Only one specimen tested	40	60
AF-40, NO PRIME, Minnesota Mining & Manufacturing Co.	Nylon-epoxy	.008 .008 .008 .008	-320	11.0 12.5 10.5 Failed Prior to Test 13.0 11.5 Avg. 11.7	-- -- -- -- --	100 100 100 -- 100 100
"	"	.010 .010 .010	-423	12.5 11.5 15.0 Avg. 13.0	-- -- --	100 100 100
AF-41, NO PRIME, Minnesota Mining & Manufacturing Co.	Nylon-epoxy	.005 .005 .005 .005 .005 .005	-320	5.0 7.0 6.0 5.0 5.0 3.5 Avg. 5.25	-- -- -- -- -- --	100 100 100 100 100 100

TABLE 3 (Continued)

Adhesive and Manufacturer*	Type	Glueline Thickness, inches	Test Temperature, °F	Tee Peel, lbs/1"	Failure % Adhesion	% Cohesion
AF-41, NO PRIME, Minnesota Mining & Manufacturing Co.	Nylon-epoxy	.005 .005 .005	-423	5.0 3.5 4.0 Avg. 4.2	-- -- --	100 100 100
FM-100, NO PRIME, Bloomingdale Rubber Co.	Nylon-epoxy	.003 .003 .002 .003 .003 .003	-320	Failed Prior to Test 3.5 2.5 3.5 3.0 3.0 Avg. 3.1	-- -- -- -- -- --	-- 100 100 100 100 100
"	"	.003	-423	Only 1 specimen 5.5 tested		100
Resin 3135, Narmco Materials Div., Tele-computing Corp.	Epoxy-poly-amide	.004 .005 .005 .005 .005 .005	-320	Zero (would not-- sustain load) " " " " Avg. Zero	-- -- -- -- --	100 100 100 100 100 100
"	"	.005	-423	Only 1 specimen tested 0 | 25		75
EC-1933B/A, Minnesota Mining & Manufacturing Co.	Filled Epoxy-poly-amide	.004 .004 .004 .004 .004	-320	1.75 1.75 2.5 1.0 1.5 Avg. 1.70	30 15 5 40 --	70 85 95 60 100
"	"	.005	-423	Only 1 specimen tested 2.25 | 20		80
APCO-1261, Applied Plastics Div., Hexcel Products Co.	Poly-ure-thane	.004 .004 .004 .004 .004 .004	-320	3.0 4.0 3.0 5.0 2.5 2.5 Avg. 3.33	-- 10 10 10 10 10	100 90 90 90 90 90

* Bonds were cured according to manufacturer's recommendations with attempt to optimize. No prime was used.

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(4) ¼" Drill Holes
Located from
Common Locating
Jig

2"

1.500"

2"

1.500"

.064" 7075T6
Bare Plate Stock
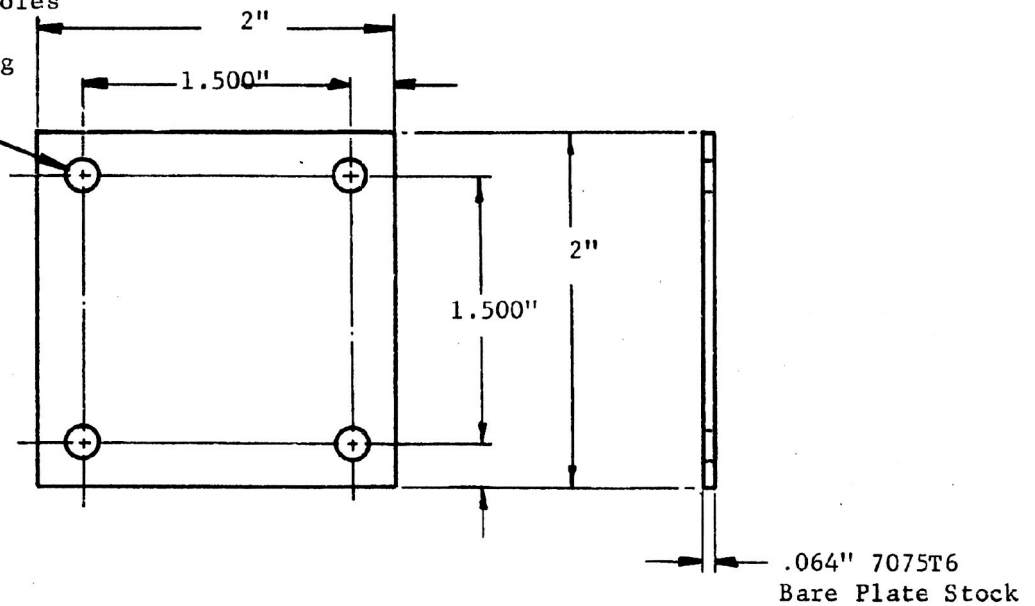
SPECIMEN A
Two Req'd

5/16" Drill

.250"

.375" ± .001"

.750"
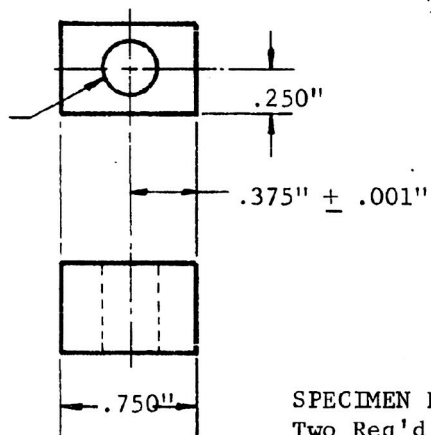
SPECIMEN B
Two Req'd

½" x 3/4"
7075T6 Bare Bar Stock

This facing
to be mach-
ined smooth,
square, &
parallel
with hole ₵
for bonding

.500"

.500"
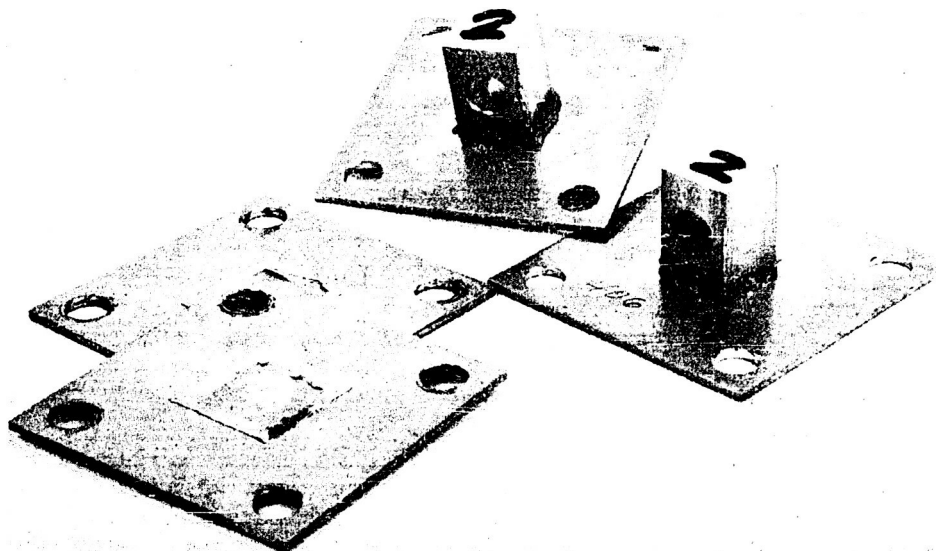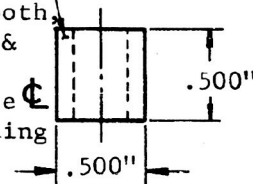
Figure 10.   Specimen design for mechanical shock tests.

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The basic machine employed for testing, exclusive of instrumentation, was the Avco SM-005-1 Shock Test Machine. Figure 11 shows the shock assembly. Modifications to the machine involved cryostating it for operation at temperatures down to -423°F. Shock pulses were obtained by the impact of the carriage assembly, which is driven downward by air pressure, against a deceleration device. Deceleration devices could include lead shot or rubber pads, depending upon the shock wave shape desired. Generation of shock pulse forms was dependent upon the weight of the specimen and carriage (28.0 pounds), this unit's velocity (drop height was 8"), and the material and configuration of the deceleration device. For these tests the deceleration device was set on rubber pads designed to give a half-sine shock pulse wave of about 6 milliseconds duration. The specimen and fixture to which it was mounted are shown in Figures 12 and 13.

The instrumentation used included an Endevco Model 2215 accelerometer, an Endevco Model 2608 cathode follower, and a Tektronix Type 543 oscilloscope equipped with a Polaroid camera. The accelerometer and cathode follower were calibrated as a system by the Endevco Corporation. The result of this calibration established a know peak millivolt output per peak "G". The oscilloscope was calibrated, with the aid of a Hewlett Packard Model 200 AB oscillator and Hewlett Packard Model 400 D vacuum tube voltmeter, for a know peak millivolt reading corresponding to the accelerometer output at the required "G" level. The oscilloscope had a calibrated time base which permitted accurate measurement of the shock pulse duration. A microswitch was used to trigger the oscilloscope at the proper time to record the shock pulse on film (see Figure 14).

Before actual testing, a great deal of effort was required for instrumentation and calibration. Many adhesive bonded specimens, including strong and weaker systems, were finally required to bring the test to the point where actual evaluation was considered justified.

It was initially intended that a set of specimens would be shocked six times at a 20-G level at -423°F, followed by removal and replacement of the specimen if it had not failed, then recalibrating and repeating the procedure at a 35, 65, and 100-G level, or until failure of the adhesive bonded specimens was attained. By this procedure a "Go" or "No Go" evaluation of each existing adhesive could be obtained. This procedure was followed for one of the nylon-epoxy existing adhesives and was carried through the 35-G level. No failure resulted. At this point it was evident that testing time and liquid hydrogen consumption would be excessive, with no assurance that the "Go" or "No Go" evaluation determined by specimen failure could be gained. It was also felt that this test might not be sufficiently severe.

In order to increase the severity of the test and reduce the testing time and consumption of liquid hydrogen, it was decided to change from a "parallel" shock to a "series" shock procedure. The "Go" or "No Go" procedure was still sought. A set of specimens bonded with the nylon-epoxy adhesive Metlbond 406 was inserted in the fixture and cooled to -423°F. The instrumentation was calibrated and a 35-G shock load applied twice. The specimens were retained in place, the instrumentation recalibrated, and a 65 G shock load applied once. Again, the specimens were retained in place, and the instrumentation recalibrated, and a 100-G shock load applied six times. As shown in Table 4, failure did not occur.
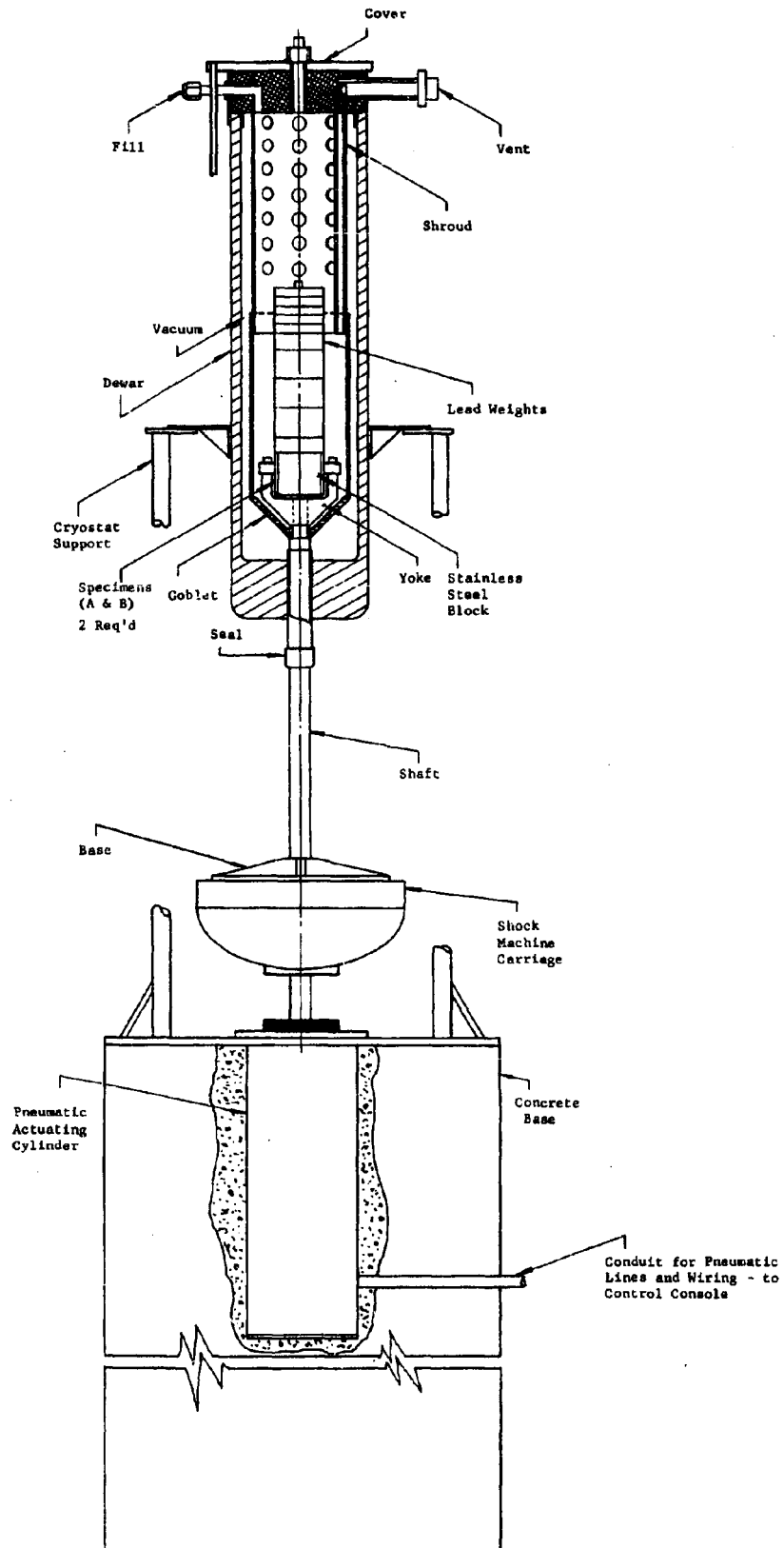
Figure 11. Mechanical Shock Assembly

Figure 12. Avco shock machine shown
with cryostat assembled, but with-
out liquid hydrogen delivery line
and purge line attached. Oscillo-
scope is shown at right. A high
speed camera for calibration
photographs the shock wave impact.
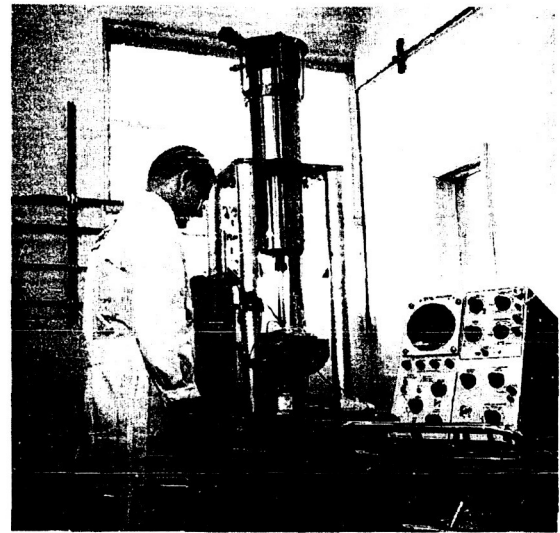
Figure 13. The console for the Avco
shock machine is also separated by
partition as a safety precaution.
The operator conducts the test by
viewing the machine through a
safety window.
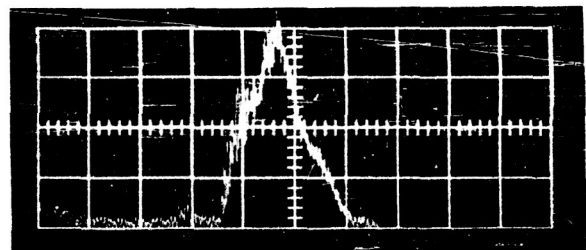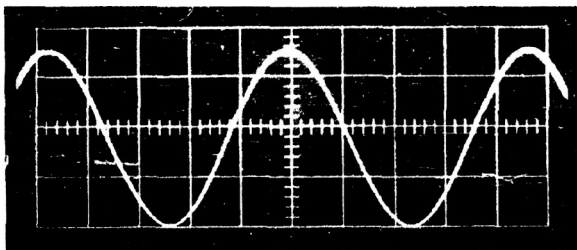
Figure 14. Wave form at left is a calibration curve for 100 G
shock test. The units on the vertical scale represent millivolt
output of a combined accelerometer-cathode follower calibrated
to a known G level. Wave form at the right is an actual 100 G
shock wave on an adhesive bonded specimen (Metlbond 406). The
units on the horizontal scale represent time duration of shock;
the largest unit (1 centimeter) is 2 milliseconds.

TABLE 4

EXISTING ADHESIVE EVALUATION

-423°F Mechanical Shock Tests
("Series" Procedure)

Adhesive and Manufacturer	Type & Glueline Thickness, inches	Wave Shape	Duration at Chassis, millisec.	Calibration G Level	Number of Shocks	Air Pressure, psi	"GO" or "NO GO"
Metlbond 406, NO PRIME, Narmco Materials Div., Tele-computing Corp.	Nylon-epoxy, .003	Half-sine	--	35	1	10	GO
			5.2	35	2	20	GO
		"	4.6	65	3	35	GO
		"	4.6	100	4	50	GO
		"	4.6	100	5	54	GO
		"	4.6	100	6	54	GO
		"	4.6	100	7	51	GO
		"	4.6	100	8	51	GO
		"	5.2	100	9	51	GO
Resin 3135, Narmco Materials Div., Tele-computing Corp.	Epoxy-poly-amide	Half-sine	--	35	1	20	GO
			6.0	35	2	20	GO
		"	--	65	3	35	GO
		"	--	65	4	35	GO
		"	--	100	5	51	NO GO

* "GO"-- No adhesive failure; "NO GO" -- Adhesive failure.

The next step in "series" shocking was to select the existing adhesive thought to have the least shock resistance (Resin 3135). As before, the set of specimens were shocked twice at a 35-G level, twice at a 65-G level, and followed by two chocks at a 100-G level. In this attempt, trouble was experienced with the scope in addition to malfunction of the device indicating failure of the specimen. Failure was thought ot have occurred on the fifth series shock. (See Table 4).

At this point it was concluded that the test was still not sufficiently severe and that failure of even the weakest of adhesives was occurring at to high a G level. It was also concluded that the test was still not sufficiently reliable to yield representative data.

Because somewhat erratic data were collected in the above shock testing at very low temperature, it was decided to test the reliability and reproducibility of the test at ambient temperature. It was anticipated that this reliability and reproducibility would be inherent in the test and carried over to very low temperature.

The "stronger" and "weaker" adhesives selected for this study were Metlbond 406 and Resin 3135/7111. The room temperature data are shown in Table 5. Metlbond 406 proved to be the more shock-resistant adhesive. Considerable scatter in data was evident, and although the test could be reproduced exactly, it was concluded that scatter was inherent in the specimen. With the 0.500 square inch bonded area involved in the specimen design, it was believed that a "Go" or "No Go" test after 6 shocks could be attained at very low temperature (-423°F) because the shock resistance would be drastically lowered from that at room temperature.

Mechanical shock tests on the developed adhesives are covered in Section XXII/ Results of mechanical shock tests at extremely low temperature were not considered completely satisfactory.

D. Thermal Shock

Initially, it was thought that thermal shock might cause premature failure of the specimen designs in this work. Tensile shear specimens of each of the existing adhesives selected were quenched from room temperature directly in liquid nitrogen. They were soaked for 10 minutes, and subsequently withdrawn and returned to ambient temperature. None of the bonds separated. A microscopic inspection of the flash area of each bond so treated did not reveal crazing or cracking. The drop in tensile shear strength from -320 to 423°F could indicate an increase in thermal stresses, as well as the expected embrittlement of the adhesive.

Frost (1) has already demonstrated that low temperature strength is not necessarily related to colling rate in arriving at a temperature of -320°F.

It was oncluded that thermal shock did not cause noticeable damage in quenching from ambient to liquid nitrogen and hydrogen temperatures, at least for the specimen designs considered here.

TABLE 5

MECHANICAL SHOCK TESTS FOR EXISTING AND NEWLY DEVELOPED ADHESIVES

(Tested at RT to show reproducibility)

Specimen Number and Adhesive	Cure	G Level	Wave Shape	Duration, milli-seconds	Air Press., psi	Number of RT Shocks
1. Resin 3135/7111	6 days RT	100	1/2 Sine	6	⌐0	25 (Failure)
2. Resin 3135/7111	3 days RT	100	1/2 Sine	6	42	48 (Failure)
3. Resin 3135/7111	3 days RT	100	1/2 Sine	6	43	154 (Failure
4. Resin 3135/7111	3 days RT	100	1/2 Sine	6	--	505 (No Failure
Resin 3135/7111	3 days RT	195	1/2 Sine	3	--	14 (Failure)
5. Metlbond 406	15 Min.@	100	1/2 Sine	6	44	200 (No Failure)
Metlbond 406	350°F	200	1/2 Sine	3	90	4 (Failure)
6. Metlbond 406	350°F	100	1/2 Sine	6	44	200 (No Failure)
Metlbond 406	350°F	200	1/2 Sine	3	90	3 (Failure)
7. Metlbond 406	350°F	100	1/2 Sine	6	44	200 (No Failure)
Metlbond 406	350°F	125	1/2 Sine	-	--	1 (No Failure)
Metlbond 406	350°F	150	1/2 Sine	-	--	1 (No Failure)
Metlbond 406	350°F	175	1/2 Sine	-	--	1 (No Failure)
Metlbond 406	350°F	180	1/2 Sine	3	90	1 (No Failure)
8. Metlbond 406	350°F	100	1/2 Sine	6	44	200 (No Failure)
Metlbond 406	350°F	137	1/2 Sine	-	--	1 (No Failure)
Metlbond 406	350°F	162	1/2 Sine	-	--	1 (No Failure)
Metlbond 406	350°F	200	1/2 Sine	3	94	1 (No Failure)

E. Coefficient of Linear Thermal Expansion

It was initially concluded that the thermal expansion, or shrinkage, of adhesives might be directly or indirectly related to such physical properties as tensile shear or peel strength. Consequently, it was decided to collect cryogenic expansion data for the existing adhesives and to analyze it.

Specimens were prepared from the adhesives by using curing times and temperatures identical with those used for preparing tensile shear and tee peel specimens. It was assumed that this would make the data easier to correlate. The "conditioning" called for in the ASTM D696-42T procedure was eliminated. In general, the film type adhesives were molded under a polyvinyl alcohol diaphragm in an autoclave at 50 psi. The paste type adhesives were centrifugally cast in a centrifuge. Specimens of film adhesives were machined to a 0.4" square cross section by 2" length. The paste materials were machined to a maximum 0.4" OD by 2" length. Bonding of steel "caps" to the end extremeties of the specimens was not accomplished.

The apparatus consisted of a #60275 Tinius-Olsen quartz tube dilatometer with the dial indicator measuring to one ten-thousandth on an inch (see Figure 15). The outside tube of the dilatometer was placed in the bottom of a glass reservoir 2" ID by 4" high, which was in turn placed in a standard 500-milliliter Pyrex beaker. The fused junction of a fine wire iron-Constantan thermocouple was taped to the side of the specimen 1" from the end with two layers of firmly wrapped masking tape. The specimen with thermocouple attached was then inserted into the dilatometer tube, the internal pushrod inserted, and the tip of the dial gage engaged with the pushrod. The reference junction was made by fusing to copper and inserting in crushed ice ($+32°F$). The copper leads were in turn connected to a #8691 Leeds Northrup millivolt potentiometer.

The dilatometer dial was adjusted to zero. The 2" ID glass reservoir was then filled with liquid nitrogen, the deflection of the dial gage being noted as the specimen contracted. The liquid nitrogen level was maintained at a heighth of 1-1/2" from the top of the glass reservoir (1/2" over the end of the specimen). Equilibrium was accepted when there was no noticeable change in dilatometer deflection or galvanometer deflection within a fifteen-minute period. The dial indicator was then reset to zero and the potentiometer read and both recorded. After the liquid nitrogen had boiled away, the temperature was monitored carefully until $+32°F$ was reached. At this point the reservoir was filled with chopped ice. Equilibrium was again attained and the dial and potentiometer readings recorded as before. The time lapse per test was approximately 2-1/2 hours. The sample length was arbitrarily recorded at room temperature. The coefficient of linear thermal expansion was calculated as follows:

$$\text{Coefficient of Linear Thermal Expansion } (-320 \text{ to } +32°F) = \frac{dL}{L_o \ (75°F) \ dT} \text{ in/in/°F}$$

where dL = Change in length over the specified temperature range, inches.

L_o = Length of the specimen measured at 75°F, inches.

dT = Temperature range, °F.
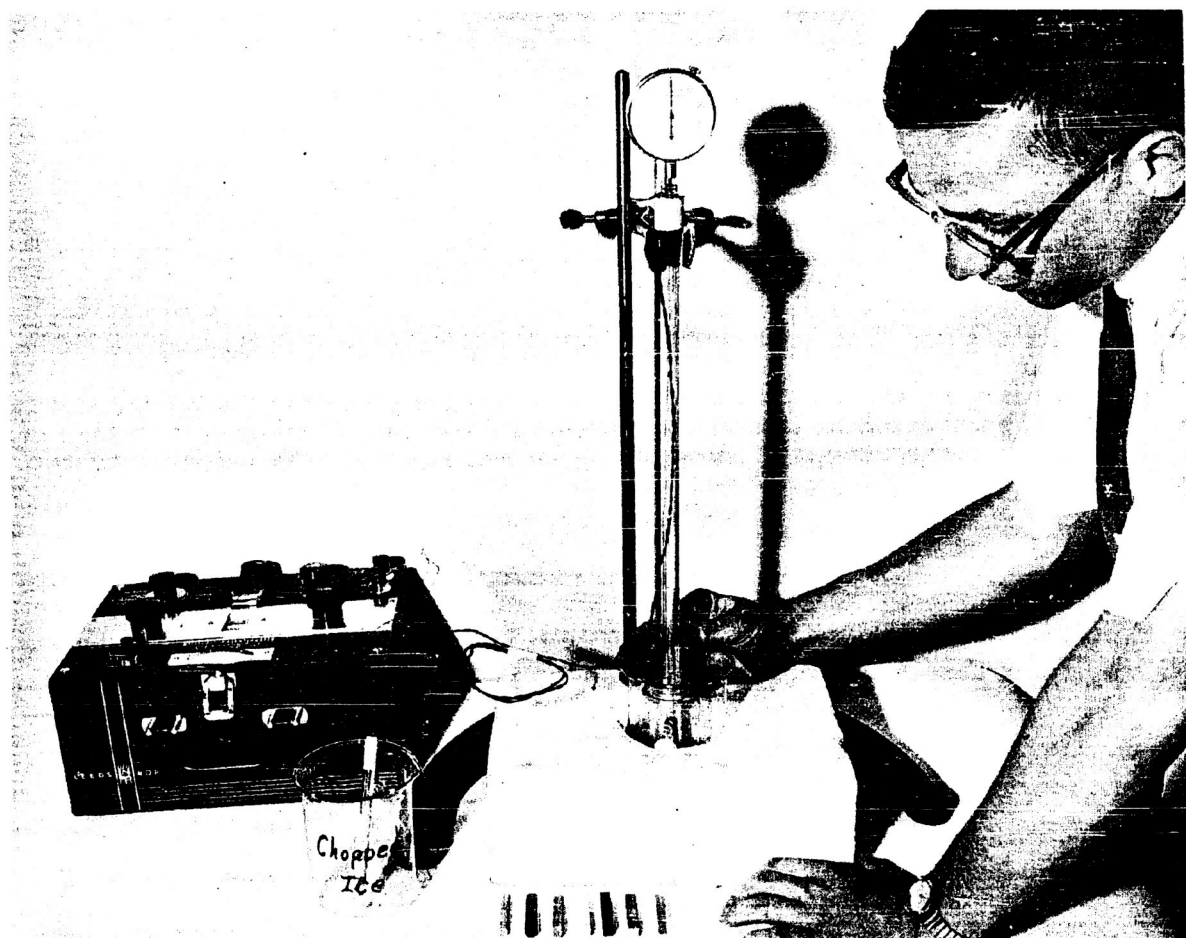
Figure 15. Test setup for measuring the coefficient of linear
thermal expansion over the temperature range from
+32 to -320°F. Included are quartz tube dilatometer,
millivolt potentiometer, and reference junction.
Initial studies employed an iron-Constantan thermo-
couple, which was later changed to copper-Constantan
for greater reliability. Adhesive specimens are
shown in foreground.

The above measurements and calculations obviously consider that the expansion is linear over the specified temperature range, and as a result the expressed coefficient of linear thermal expansion is an average over the temperature range. Actually, the expansion is not quite linear over the -320°F temperature range. This is probably due to the fact that at any instantaneous point it is almost impossible to attain equilibrium conditions as the temperature rises or falls. It is not possible to maintain a linear heat rise or fall with respect to time over such a wide range because of the nonoverlapping boiling points of available cryogenic fluids. Transition points also account for non-linearity. In fact, a hysteresis is observed between the temperature range, depending upon whether instantaneous data are collected when the specimen is being warmed or cooled. Apparently differential thermal transfer errors influence the results when non-equilibrium conditions exist.

Table 6 gives the coefficients of linear thermal expansion for two separate specimens of each existing adhesive. The mean deviation is also calculated. As explained above, the data are presented as an average over the temperature range specified.

Considerable effort has been made to correlate these data with physical properties such as tensile shear and peel strength. No satisfactory correlation has been found at the present time. It is interesting to note that the coefficient for Metlbond 408 is greater than that for Metlbond 406. This was quite unexpected. The composition for these materials is represented schematically as follows:

Adhesive	% Nylon	% Epoxy
Metlbond 406	High	Low
Metlbond 408	Lower	Higher

With Nylon having a higher coefficient of expansion than epoxy resins (2), it is normally expected that the coefficient for metlbond 406 will be higher than that for Metlbond 408. Other factors, such as, crystallinity, degree of cure, adhesive processing methods, etc., can influence this. Further treatment of expansion is given in Section XI.

V. INITIAL STUDY OF METAL SURFACE TREATMENTS FOR ADHESIVE BONDING AT EXTREMELY LOW TEMPERATURE

It is a well established fact that the surface treatment to which adherend materials are subjected prior to adhesive bonding greatly influences the strength of the bonded assembly. It was anticipated that there probably would be an optimum surface treatment for each of the metals, which would demonstrate good adhesion and toughness for application in the cryogenic environment. Obviously, a surface treatment for a particular metal could show optimum bonding characteristics at ambient or elevated temperature, but might become too brittle or have too high a modulus for optimum bonding at cryogenic temperatures.

TABLE 6

COEFFICIENT OF LINEAR THERMAL EXPANSION
DEVELOPED FOR EXISTING ADHESIVES AT CRYOGENIC TEMPERATURES

Adhesive	Coefficient of Linear Thermal Expansion (-320 to +32°F), inches/inch/°F x 10^{-5}			Percent Deviation*
	Sample #1	Sample #2	Average	
APCO-1261	4.12	4.07	4.10	1.22
Metlbond 408	3.33	3.15	3.24	5.55
AF-40	3.11	3.04	3.08	2.27
Metlbond 406	3.15	2.98	3.06	5.55
Resin 3135	3.22	3.21	3.21	0.31
FM-1000	2.91	2.85	2.88	2.08
AF-41	2.84	2.74	2.79	3.59
EC-1933B/A	2.38	2.19	2.28	8.33

* Deviation from arithmetic mean.

Two adherends were selected for this study: 7075T6 bare aluminum alloy and 17 - 7 PH stainless steel. Treatments for the former consisted of the following: methyl ethyl ketone degrease, sandblast, standard FPL sodium dichromate sulfuric acid etch, Alodine, and anodize. Treatments for the latter consisted of the following: methyl ethyl ketone degrease, sandblast, phosphate, hydrogen peroxide, and Prebond 700.

Metlbond 406 (nylon epoxy film) was the adhesive selected for evaluation against each surface treatment. Tensile shear data were collected at +260°F, RT, and -320°F. The manufacturer's recommendations for bonding were followed without attempts to optimize.

Table 7 presents the data collected in this study. Although the anodize surface treatment for 7075T6 bare aluminum yielded the best bonding surface at -320°F of those studied, the sandblast treatment is the most practical from the standpoint of ease of preparation and it is the closest equivalent. The hydrogen peroxide surface treatment yielded the best surface treatment at -320°F of those studied for 17 - 7 PH stainless steel, but, the sandblast surface again is more practical and a very close equivalent. Surface treatment studies are described further in Section XX.

Phosphate Treatment - Mythyl ethyl ketone degrease. Ajax scrub.
Water rinse. Immerse 2 minutes in following solution at 90°C:
    280 ml. hydrochloric acid (35%)
     30 ml. phosphoric acid (85-87%)
     16 ml. hydrofluoric acid (48%)
Follow with tap water rinse, distilled water rinse, and oven dry at 180°F.

Hydrogen Peroxide Treatment - Methyl ethyl ketone degrease.'
Immerse 10 minutes in following solution at 150°F:
    100 gms. hydrochloric acid (35%)
      4 gms. hydrogen peroxide (30%)
     20 gms. formalin (40%)
     90 gms. distilled water.
Follow with tap water rinse and distilled water rinse. Air dry.
Etch 5-10 minutes at 140-160°F in following solution:
    100 gms. sulfuric acid (98%)
     10 gms. sodium dichromate
     30 gms. distilled water
Repeat rinse and drying procedures immediately above.

VI. PROCESSING STUDIES FOR NYLON-EPOXY ADHESIVE COMPOSITIONS

There are several means for combining the nylon and epoxy constituents of an adhesive such as Metlbond 406: namely, dry mixing on a rubber mill, casting from solution or dispersion, mixing from gelled solutions or dispersions on a rubber mill, or mixing in a fused state on a hot rubber mill.

These four processes were applied to the Metlbond 406 nylon-epoxy adhesive formulation and the resultant adhesive films were used for the preparation of 1/2" overlap joints with .064" 7075T6 bare aluminum adherends. The -320°F and RT tensile shear strengths of the bonds were studied.

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TABLE 7

STUDY OF METAL SURFACE TREATMENTS FOR ADHESIVE BONDING AT EXTREMELY LOW TEMPERATURE

Metal	Surface Treatment	Tensile Shear Strength, psi											
		+260°F				R.T.				-320°F			
		GLT	Psi	% Adh.	% Coh.	GLT	Psi	% Adh.	% Coh.	GLT	Psi	% Adh.	% Coh.
7075T6 Bare Aluminum	Methyl Ethyl Ketone Degrease	.002	350	100	--	.004	3460	60	40	.001	1760	60	40
		.003	334	100	--	.004	2750	60	40	.003	1054	100	--
		.004	396	100	--	.004	2100	80	20	.003	682	100	--
		.004	320	100	--	.005	2370	90	10	.004	958	100	--
		.003	316	100	--	.005	1880	100	--	.003	934	100	--
		.002	420	100	--	.004	2020	90	10	.003	874	100	--
		.003	268	100	--	.004	2510	90	10	.002	1186	100	--
		.002	220	100	--	.004	2660	80	20	.002	2280	75	25
			Avg.328				Avg.2468				Avg.1216		
Same	Sand Blast	.002	316	90	10	.002	3800	50	50	.002	3600	100	--
		.002	316	90	10	.003	3940	60	40	.002	3560	100	--
		.001	464	90	10	.003	4500	50	50	.002	3660	100	--
		.001	472	100	--	.003	4580	60	40	.002	3540	100	--
		.002	426	100	--	.003	4200	50	50	.001	3670	100	--
		.002	450	100	--	.004	4660	50	50	.001	3500	100	--
		.002	356	100	--	.003	4020	50	50	.001	3860	100	--
		.001	300	100	--	.003	2620	50	50	.001	3890	100	--
			Avg.387				Avg.4040				Avg.3660		
Same	FPL Sodium Di-chromate Sulfuric Acid Etch	.004	536	60	40	.004	5600	40	60	.002	4080	60	40
		.003	558	80	20	.003	6720	20	80	.003	3250	60	40
		.004	606	80	20	.003	7040	30	70	.004	3250	70	30
		.004	586	60	40	.003	6680	50	50	.004	3710	60	40
		.004	628	80	20	.003	6680	30	70	.004	3680	60	40
		.004	664	60	40	.003	6200	20	80	.003	3510	70	30
		.003	602	60	40	.003	5560	20	80	.003	3440	90	10
		.003	516	60	40	.003	6400	20	80	.003	4960	60	40
			Avg.587				Avg.6360				Avg.3735		

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TABLE 7 (Continued)

Tensile Shear Strength, psi

Metal	Surface Treatment	+260°F				R.T.				-320°F			
		GLT	Psi	% Adh.	% Coh.	GLT	Psi	% Adh.	% Coh.	GLT	Psi	% Adh.	% Coh.
Same	Alodine	.003	350	90	10	.002	3600	75	25	.002	580	100	--
		.003	452	100	--	.002	3680	75	25	.002	600	100	--
		.003	384	90	10	.002	2800	75	25	.002	1440	100	--
		.003	444	100	--	.002	2600	60	40	.002	1394	100	--
		.003	444	100	--	.002	3520	80	20	.002	1162	100	--
		.003	458	90	10	.002	3560	75	25	.002	1052	100	--
		.002	260	90	10	.002	3000	75	25	.002	1020	100	--
		.002	230	90	10	.002	3120	70	30	.002	574	100	--
			Avg.379				Avg.3235				Avg.977		
7075T6 Bare Aluminum	Anodize	.001	474	70	30	.002	4240	50	50	.001	5060	Metal	
		.001	836	80	20	.003	5040	50	50	.002	4260	60	40
		.001	782	60	40	.002	5960	50	50	.003	3650	60	40
		.001	892	50	50	.002	6840	50	50	.004	3620	100	--
		.001	400	80	20	.003	6920	50	50	.003	4120	50	50
		.001	970	70	30	.003	6280	50	50	.001	5880	Metal	
		.001	1156	50	50	.002	5880	50	50	.002	5110	50	50
		.001	814	60	40	.003	6000	50	50	.001	5830	Metal	
			Avg.790				Avg.5895				Avg.4691		
17-7 PH Stainless Steel	Methyl Ethyl Ketone Degrease	.008	300	100	--	.004	4440	50	50	.006	4340	100	--
		.008	538	100	--	.007	4140	45	55	.007	3330	100	--
		.009	486	100	--	.008	4360	45	55	.009	3770	100	--
		.009	498	90	10	.007	4440	30	70	.010	3880	100	--
		.009	400	80	20	.009	4220	30	70	.009	3100	90	10
		.009	364	100	--	.009	3860	40	60	.010	3770	90	10
		.009	450	100	--	.008	3860	50	50	.011	2360	100	--
		.007	304	90	10	.007	4300	30	70	.007	2340	100	--
			Avg.417				Avg.4202				Avg.3298		

(Continued on next page)

TABLE 7 (Continued)

Tensile Shear Strength, psi

Metal	Surface Treatment	+260°F GLT	+260°F Psi	+260°F % Adh.	+260°F % Coh.	RT GLT	RT Psi	RT Adh.	RT % Coh.	-320°F GLT	-320°F Psi	-320°F % Adh.	-320°F % Coh.
Same	Sand Blast	.002	204	75	25	.003	4760	50	50	.002	3960	-	100
		.001	206	95	5	.002	4720	60	40	.001	4820	-	100
		.001	206	85	15	.002	4600	60	40	.001	5070	-	100
		.001	212	85	15	.002	4760	70	30	.002	4860	-	100
		.001	208	85	15	.002	4520	70	30	.002	4840	Metal	
		.001	200	85	15	.002	4680	75	25	.001	4840	Metal	
		.001	218	85	15	.002	4760	75	25	.002	5440	-	100
		.001	192	90	10	.002	4720	70	30	.002	6250	-	100
			Avg. 205				Avg. 4690				Avg. 5008		
Same	Phosphate	.003	516	75	25	.002	4160	25	75	.004	2240	100	-
		.004	412	90	10	.003	4320	25	75	.003	2770	100	-
		.004	276	75	25	.003	4080	40	60	.001	2530	100	-
		.004	280	70	30	.003	4520	40	60	.007	2230	100	-
		.004	568	70	30	.005	2800	40	60	.006	2100	100	-
		.004	588	80	20	.003	4400	40	60	.006	2140	100	-
		.002	398	90	10	.004	4160	40	60	.004	2190	100	-
		.002	210	85	15		4320	40	60	.004	2040	100	-
			Avg. 406				Avg. 4095				Avg. 2280		
17-7 PH Stainless Steel	Hydrogen Peroxide	.005	380	95	5	.006	4440	25	75	.004	5980	100	-
		.006	390	90	10	.007	4040	25	75	.005	5330	Metal	
		.007	320	95	5	.006	4200	30	70	.008	4630	Metal	
		.009	200	100	--	.006	4240	30	70	.005	6230	100	-
		.011	80	100	--	.004	3800	30	70	.004	3800	100	-
		.003	376	100	--	.004	4000	40	60	.004	5780	Metal	
		.001	188	100	--	.004	4200	40	60	.003	6020	100	-
		.002	276	95	5	.004	4080	40	60	.005	5800	100	-
			Avg. 276				Avg. 4125				Avg. 5446		

TABLE 7 (Continued)

Tensile Shear Strength, psi

Metal	Surface Treatment	+260°F				R.T.				-320°F			
		GLT	Psi	% Adh.	% Coh.	GLT	Psi	% Adh.	% Coh.	GLT	Psi	% Adh.	% Coh.
Same	Prebound 700	.004	964	100	--	.006	4700	50	50	.004	4520	--	100
		.004	1012	100	--	.008	4200	50	50	.012	1510	--	100
		.006	1430	100	--	.008	4480	50	50	.008	4250	--	100
		.007	1360	100	--	.009	4820	40	60	.007	4020	--	100
		.008	1340	100	--	.008	4580	50	50	.008	4170	--	100
		.007	1136	100	--	.008	3300	50	50	.008	4220	--	100
		.006	850	100	--	.004	4860	50	50	.004	4310	--	100
		.005	836	100	--	.005	4420	50	50	.006	1550	--	100
			Avg 1116				Avg 4420				Avg 3568		

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Table 8 shows that the processing method definitely influences the low temperature strength of the adhesive. Cold mixing from gelled solutions or dispersions (solution mixing, calendering) appear preferred for all test conditions. Dry mixing on a rubber mill and casting from solution or dispersion are almost equivalent and fall next in line.

VII. COMPARISON OF EPOXY WITH OTHER RESIN SYSTEMS AS REINFORCING AGENTS FOR NYLON-BASED ADHESIVES FOR APPLICATION AT VERY LOW TEMPERATURE

Although the nylon-epoxy systems have performed exceedingly well as structural adhesives at very low temperature, it was felt that other resin systems (phenolic, acrylic, polyester, and polyurethane) should be evaluated as reinforcing agents for nylon. The ultimate goal was a resin system that might perform more advantageously at low temperature than epoxy resins. Included in the study were various weight ratios of resin reinforcing agent to nylon, i.e., 25/75, 50/50, and 75/25.

The specific resins chosen and their formulations are given below:

Epoxy   Phenolic   Acrylic

DER 331   BRL 2741   Lucite 204-X
Dicyandiamide 6 phr   Benzoyl peroxide 1%
(pre-reacted to a gel
time of 5 minutes at
350°F)

            Polyester   Polyurethane

            Vibrin 136A   Apco 1261 Part A
            t-butyl Perbenzoate   Apco 1261 Part B
            0.2 phr   (equal parts by weight)

Zytel 61 was chosen as the nylon copolymer for the study. This was dissolved in ethyl alcohol to make a solution approximately 40% solids. The required amount of prereacted epoxy resins was dissolved in methyl ethyl ketone to make a solution approximately 20% solids. This solution, thoroughly mixed, was added to the required amount of nylon solution at 150°F to yield a good suspension or dispersion. The resultant suspension was immediately knife-coated on separator paper and allowed to air dry. Once a film had formed, the air dry was followed by an oven dry of 1/2 hour at 180°F for solvent release. The adhesive film was stripped from the casting paper and used for bonding.

The required amount of phenolic resin was dissolved in the required amount of nylon solution and the mixture applied directly to the faying surfaces of the adherends. A vacuum oven dry (30" Hg at 180°F) was employed for final solvent release prior to bonding. The remaining resins were handled in a similar manner, with the exception that the acrylic was dissolved in ethylene dichloride and the drying temperature maintained at RT. The polyester was dissolved in methyl ethyl ketone, and the polyurethane was added directly to the nylon solution.

TABLE 8

PROCESSING STUDIES FOR
NYLON-EPOXY ADHESIVE COMPOSITIONS

Compound Process	Tensile Shear, psi		
	+260°F*	R.T.**	-320°F**
Dry Mixing Calendering (Standard Metlbond 406 Process)	420	4722	3450
Solution Casting	531	5342	3512
Solution Mixing, Calendering	1602	6257	4057
Fused Mixing, Calendering	723	4806	2950

Cured by staging from R.T. to 350°F in 20 minutes and holding
1 hour at 350°F and 25 psi.

* Average of 4 specimens

** Average of 8 specimens

Table 9 shows the results of this study. The epoxy resin was far superior as a reinforcing agent for nylon, in terms of tensile shear and peel strengths both at room temperature and at -320°F, than any of the other four resins studied. This might have been due to the epoxide groups co-reacting with the amide groups on the surface of the nylon. The very poor reinforcing effects of the phenolic resin were probably due to the solvent effects of phenolics on nylon, which completely breaks up the desirable nylon structure. The poor effects of the acrylic and polyester were probably due, in part, to the partial incompatibility of these resins with nylon. The polyurethane was found to be completely incompatible with nylon.

VIII. A STUDY OF NYLON POLYMER AND COPOLYMER CHEMICAL STRUCTURE TO OPTIMIZE ADHESIVE STRENGTH AT EXTREMELY LOW TEMPERATURE

A. Nylon Fillers for Epoxy-Polyamides

Because of the extremely interesting low-temperature properties demonstrated by nylon in adhesive applications (used either as fillers or prime adhesive constituents) it was decided that it would be very worthwhile to study structure and determine the effect of different nylon chemical structures on adhesion. A series of nylons was prepared in the laboratory especially for adhesive application. It was felt necessary to include in the polymer or copolymer structures various degrees of hydrogen bonding, various carbon chain lengths between amide groups, and aromatic as well as aliphatic chain constituents in an attempt to 1) increase compatibility with resin systems such as epoxies, 2) to decrease softening points, 3) to increase solubility, and 4) to enhance the low temperature characteristics.

The action of acid chlorides of dibasic acids (diacyl chlorides) on diamines, via the route of the well-established art of interfacial polymerization, was selected because of the easily obtained, high-molecular weight polymers. These highly reactive monomers preclude the need for the very rigorous autoclave conditions required when dibasic acids and diamines are employed as monomers with attendant difficulty in controlling the degree of polymerization or molecular weight.

Approximately 0.05 mol of the acid chloride, or combined acid chlorides, was dissolved in 50 ml benzene. An equivalent molar amount of diamine, or combined diamines, was dissolved in 50 ml of water. The two solutions were combined and mixed, yielding immediately a large coagulated mass of polymer. The polymeric mass was divided into small particle sizes and washed repeatedly with warm benzene to remove entrained monomer. This was followed by repeated washings with hot ethanol/water (80/20) solutions to further remove monomer and lower molecular weight fragments. The resulting polymer was dried in a vacuum oven to remove solvent.

The final step consisted of grinding the polymer in a mortar and pestal under liquid nitrogen and screening it through a 200-mesh sieve.

Evaluation of the polymer consisted of 1) determining the softening point by parallel plate plastometry, and 2) employing the finely divided polymer as a filler for a epoxy-polyamine adhesive (Resin 3135).

TABLE 9

COMPARISON OF EPOXY WITH OTHER RESIN SYSTEMS AS REINFORCING AGENTS
FOR NYLON-BASED ADHESIVES FOR APPLICATION AT VERY LOW TEMPERATURE

Code	Adhesive System	Ratios	Tensile Shear, psi*		Tee Peel, lbs/1"**	
			R.T.	-320°F	R.T.	-320°F
58	Nylon/Epoxy	25/75	3910	2632	10.0	4.0
59	" "	50/50	6110	2728	50.0	5.0
60	" "	75/25	7455	3079	65.0	7.5
61	Nylon/Phenolic***	25/75	1195	1288	0	0.5
62	" · "	50/50	1820	1311	0	1.0
63	" "	75/25	2708	1977	1.0	1.0
64	Nylon/Acrylic	25/75	1526	1640	5.0	1.5
65	" "	50/50	2210	3000	22.5	2.5
66	" "	75/25	2555	1312	30.0	2.0
67	Nylon/Polyester	25/75	1662	780	0	0.5
68	" "	50/50	1651	1066	0	0.5
69	" "	75/25	1356	1034	5.0	2.0
		(#67, 68 and 69 Systems partially incompatible)				
70	Nylon/Polyurethane	25/75	Systems completely incompatible			
71	" "	50/50	"	"	"	
72	" "	75/25	"	"	"	

* Average of four specimens

** Single specimens

*** Cure staged from RT to 225°F in 20 minutes, 45 min at 225°F at 25 psi,
staged from 225°F to 350°F, 1 hour at 350°F and 25 psi.

All cures were 1 hour at 350°F and 25 psi, except where noted.

The polymer was pelletized into a specimen approximately 1/4" diameter by 1/8" thick for softening point determinations. The parallel plate plastometer was constructed from a standard Fisher-Johns melting point apparatus (see Figure 16) which was connected in series with a powerstat to slow down the heating rate. The pelletized polymer specimen was placed between standard glass cover plates, positioned on the platen of the apparatus, and loaded with a 1/2" diameter steel rod weighing 332 grams. The end of the rod was engaged with a dial indicator for measuring deflection. Heating of the apparatus was begun at a controlled rate, 4°C per minute, and temperature and deflection recorded. Heating was continued until no further deflection could be observed. A plot of temperature (abscissa) vs. deflection (ordinate) was made and the softening point chosen at the point on the abscissa where the radical change in deflection was observed. The resulting temperature was reported as the softening point, °C.

Three polymers, whose softening points are well-established, were prepared to prove the quality of the polymer. The nylon from hexamethylene diamine and adipoyl chloride and the nylon from hexamethylene diamine and sebacoyl chloride gave precisely the literature-reported (3) softening points 260°C and 209°C,respectively, when prepared from the diamines and dibasic acids. The softening point for nylon copolymer from hexamethylene diamine and mixed adipoyl and sebacoyl chloride was somewhat higher (219°C) than the literature-reported(4) value of 200°C. It was concluded that the polymers produced by the reaction were of high molecular weight and good quality.

Twenty-nine other polymers and copolymers were prepared by the reaction described. Table 10 gives their composition and softening points. Using the softening point of Zytel 61 as control (138°C), it was concluded that all (with the exception of polymers #18 and #48) had too high a softening point to be considered practical in a nylon-epoxy adhesive such as Metlbond 406, AF-40 or AF-41, or FM-1000, because these adhesives require fusion of the nylon for adhesion. Obviously, fusion takes place at temperatures higher than the softening point, and softening temperatures above 138°C would require curing temperatures in excess of 350°F. This would be a disadvantage in the present work because of the more moderate curing conditions required.

Due to the excellent results nylons have shown as fillers for epoxy-polyamine adhesives and because of the high softening points, the majority of these nylon polymers and copolymers were tested as fillers for Resin 3135. The same procedures described in the preceding section for adhesive and bond preparation were followed. The resultant test data are given in Table 10. It was noted that all of the polymers or copolymers evaluated as fillers did not perform as well as Zytel 61 in either RT or -320°F tensile shear strength. Some demonstrated an improvement in RT tee peel strength; nevertheless, the -320°F tee peel strength was not improved over Zytel 61 as the control.

It was observed that some of the polymers and copolymers had greater thickening effects of Resin 3135 than other polymers when used at 33.3 parts per hundred parts. This influenced the glueline thickness of the bonded specimens as well as the adhesive's ability to wet the faying surfaces. It was difficult to control the curing time at room temperature of the bonded assemblies prior to testing. Times actually ranged from 48 hours to 10 days. Figure 17 is submitted to identify the curing time for each system. Although not a justified correlation, the -320°F tensile shear strength tends to increase with curing time at RT.
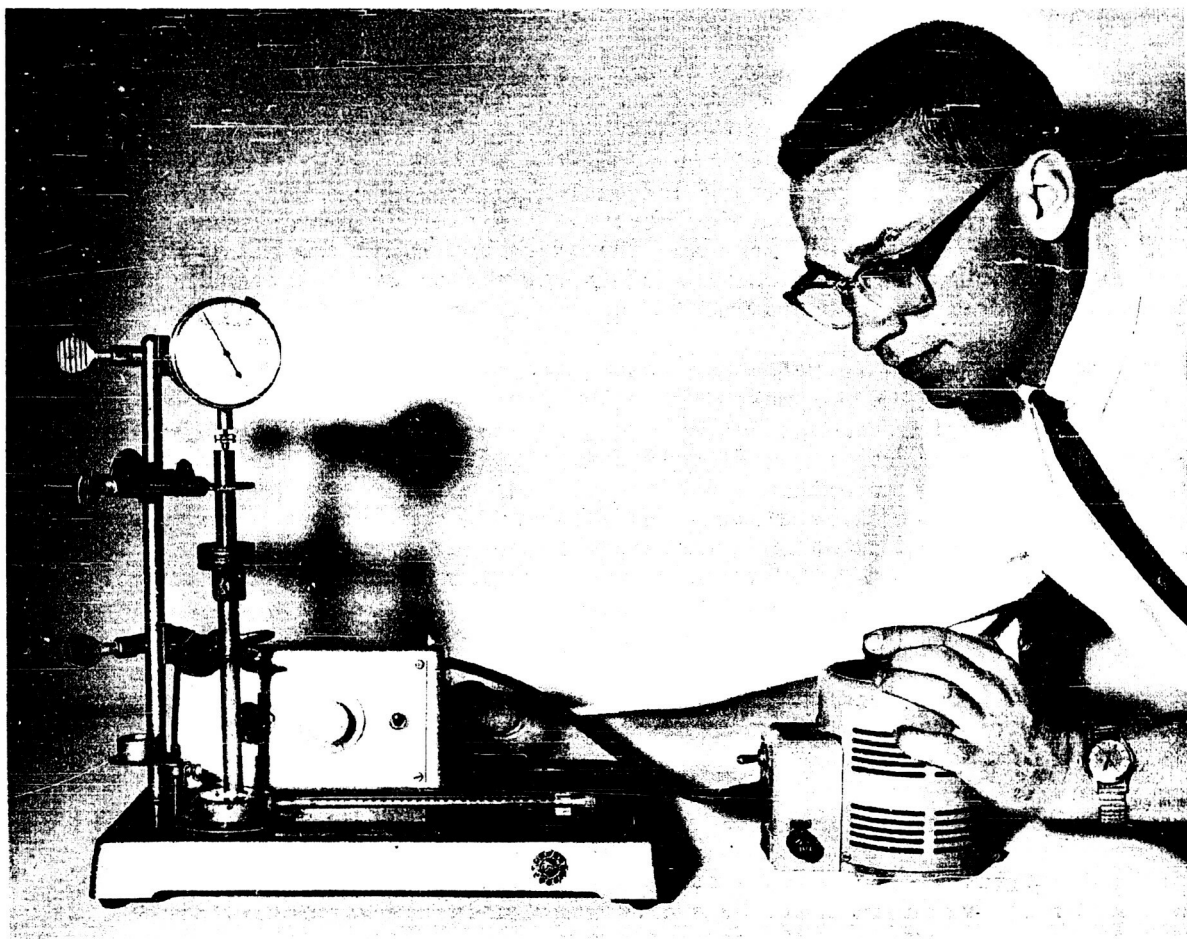
Figure 16. Parallel plate plastometer fashioned from a Fisher-Johns melting point apparatus and used for determining the softening point of nylon polymers and copolymers.

TABLE 10

A STUDY OF NYLON POLYMER AND COPOLYMER CHEMICAL STRUCTURE TO OPTIMIZE ADHESIVE STRENGTH AT EXTREMELY LOW TEMPERATURE

Polymers and Copolymers Used as Fillers for Resin 3135

Code No.	Nylon Monomeric Constituents	Softening Point, °C	Adhesive Compositions -- Resin 3135 Filled with 33.3 phr Nylon (200 mesh)			
			Tensile Shear*, psi		Tee Peel**, lbs/1"	
			R.T.	-320°F	R.T.	-320°F
	Aliphatic Nylons					
CONTROL	Zytel 61 (Dupont)	138	3140	3180	2.0	2.5
1	0.05 Mol Hexamethylene Diamine 0.05 Mol Adipoyl Chloride	260(260***)	2263	2517	2.5	1.0
2	0.05 Mol Hexamethylene Diamine 0.05 Mol Sebacoyl Chloride	209(209***)	2055	2242	2.5	1.5
3	0.05 Mol Hexamethylene Diamine 0.05 Mol Oxaloyl Chloride	320	--	--	-	-
4	0.05 Mol Ethylene Diamine 0.05 Mol Adipoyl Chloride	280	370	567	3.5	1.0
5	0.05 Mol Ethylene Diamine 0.05 Mol Sebacoyl Chloride	254	1054	1137	3.5	0.5
6	0.05 Mol Ethylene Diamine 0.05 Mol Oxaloyl Chloride	>290 Decomposes	--	--	-	-
36	0.05 Mol Hexamethylene Diamine 0.05 Mol Azelaoyl Chloride	181	1444	1276	5.0	2.0
37	0.05 Mol Ethylene Diamine 0.05 Mol Azelaoyl Chloride	221	1295	1944	4.5	2.5
21	0.05 Mol Hexamethylene Diamine 0.025 Mol Adipoyl Chloride 0.025 Mol Sebacoyl Chloride	219(200***)	2112	1757	2.5	1.0
30	0.05 Mol Ethylene Diamine 0.025 Mol Adipoyl Chloride 0.025 Mol Sebacoyl Chloride	226	--	--	-	-
34	0.025 Mol Ethylene Diamine 0.025 Mol Hexamethylene Diamine 0.05 Mol Sebacoyl Chloride	194	854	1114	5.0	1.5

(Continued on next page)

* Cured approximately 48 hours at RT. Tested per MIL-A-5090D. Average of four specimens.
** Cured approximately 48 hours at RT. (See Figure 20). Single specimen
*** Data reported in the literature.

TABLE 10 (Continued)

Code No.	Nylon Monomeric Constituents	Softening Point, °C	Adhesive Compositions -- Resin 3135 Filled with 33.3 phr Nylon (200 mesh)			
			Tensile Shear*, psi		Tee Peel**, lbs/1"	
			R.T.	-320°F	R.T.	-320°F
40	0.05 Mol Hexamethylene Diamine 0.025 Mol Adipoyl Chloride 0.025 Mol Azelaoyl Chloride	237	--	--	-	-
41	0.05 Mol Hexamethylene Diamine 0.025 Mol Azelaoyl Chloride 0.025 Mol Sebacoyl Chloride	181	--	--	-	-
47	0.025 Mol Ethylene Diamine 0.025 Mol Hexamethylene Diamine 0.025 Mol Adipoyl Chloride 0.025 Mol Sebacoyl Chloride	195	924	1132	7.5	2.0
49	0.10 Mol Ethylene Diamine 0.10 Mol Hexamethylene Diamine 0.10 Mol Azelaoyl Chloride 0.10 Mol Sebacoyl Chloride	152	998	1620	5.0	2.0
Aromatic Nylons						
7	0.05 Mol Hexamethylene Diamine 0.05 Mol Terephthaloyl Chloride	389	2128	2017	2.5	2.0
8	0.05 Mol Hexamethylene Diamine 0.05 Mol Isophthaloyl Chloride	165	2545	1166	Failed in Handling	2.5
9	0.05 Mol Ethylene Diamine 0.05 Mol Terephthaloyl Chloride	380	600	796	2.5	1.0
10	0.05 Mol Ethylene Diamine 0.05 Mol Isophthaloyl Chloride	255	1202	1182	2.5	0.5
11	0.025 Mol Ethylene Diamine 0.025 Mol Hexamethylene Diamine 0.05 Mol Terephthaloyl Chloride	380	898	1046	3.5	1.0
12	0.025 Mol Ethylene Diamine 0.025 Mol Hexamethylene Diamine 0.05 Mol Isophthaloyl Chloride	222	--	--	-	-
13	0.05 Mol Hexamethylene Diamine 0.025 Mol Isophthaloyl Chloride 0.025 Mol Terephthaloyl Chloride	288	--	--	-	-

(Continued on next page)

* Cured approximately 48 hours at RT. Tested per MIL-A-5090D.
** Cured approximately 48 hours at RT. (See Figure 20). Single specimen.

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TABLE 10 (Continued)

Code No.	Nylon Monomeric Constituents	Softening Point, °C	Adhesive Compositions -- Resin 3135 Filled with 33.3 phr Nylon (200 mesh)			
			Tensile Shear*, psi		Tee Peel**, lbs/1"	
			R.T.	-320°F	R.T.	-320°F
14	0.05 Mol Ethylene Diamine 0.025 Mol Isophthaloyl Chloride 0.025 Mol Terephthaloyl Chloride	237	--	--	--	--
	Mixed Aliphatic and Aromatic Nylons					
15	0.05 Mol Hexamethylene Diamine 0.025 Mol Adipoyl Chloride 0.025 Mol Terephthaloyl Chloride	337	1270	1634	6.2	1.0
16	0.05 Mol Hexamethylene Diamine 0.025 Mol Sebacoyl Chloride 0.025 Mol Terephthaloyl Chloride	325	1209	1760	5.0	2.5
18	0.05 Mol Hexamethylene Diamine 0.025 Mol Adipoyl Chloride 0.025 Mol Isophthaloyl Chloride	138	3085	1757	0	1.0
19	0.05 Mol Hexamethylene Diamine 0.025 Mol Sebacoyl Chloride 0.025 Mol Isophthaloyl Chloride	197	1328	744	7.5	1.5
28	0.05 Mol Ethylene Diamine 0.025 Mol Sebacoyl Chlcride 0.025 Mol Isophthaloyl Chloride	257	--	--	--	--
38	0.05 Mol Hexamethylene Diamine 0.025 Mol Azelaoyl Chloride 0.025 Mol Terephthaloyl Chloride	334	1626	1820	5.0	2.0
39	0.05 Mol Hexamethylene Diamine 0.025 Mol Azelaoyl Chloride 0.025 Mol Isophthaloyl Chloride	204	2932	1457	3.5	2.5
48	0.025 Mol Ethylene Diamine 0.025 Mol Hexamethylene Diamine 0.025 Mol Adipoyl Chloride 0.025 Mol Isophthaloyl Chloride	30	--	--	--	--
50	0.10 Mol Ethylene Diamine 0.10 Mol Hexamethylene Diamine 0.10 Mol Azeloyl Chloride 0.10 Mol Terephthaloyl Chloride	369	782	1244	5.0	2.0

* Cured approximately 48 hours at R.T. Tested per MIL-A-5090D. Average of four specimens.

** Cured approximately 48 hours at R.T. (See Figure 20). Single specimen.
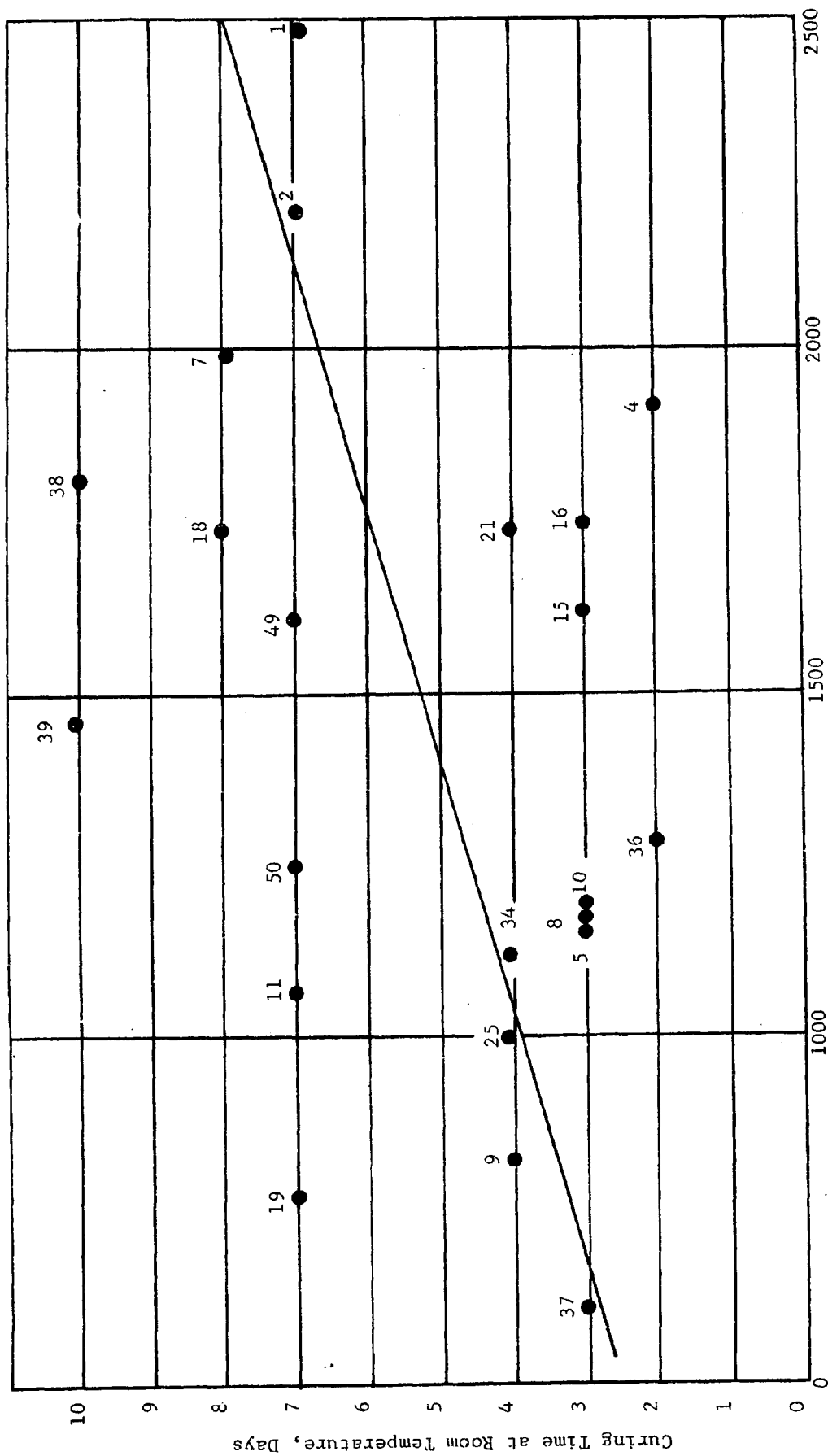
Figure 17. RT curing time vs. -320°F tensile shear strength of Narmco Resin 3135 filled with a series of different nylon polymers and copolymers

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B. Nylon Epoxy Adhesives

Based upon the comparatively low softening points of polymers #18 and #48 in the foregoing study (138°C and 30°C, respectively), it was decided to explore nylon structure further in adhesive systems where the polymer is the prime adhesive constituent requiring fusion during bonding for optimum properties. It was hoped that the low temperature properties of nylon might be improved as a result of their low softening points.

The Metlbond 406 formulation (processed by dry mixing and calendering) was selected as the basis for evaluating the two nylons mentioned above and three additional nylons. Numbers 52 and 53 were especially prepared by allowing blends of two different polyamides to co-react when heated above the melting point, first to give block copolymers, followed by segment interchange leading to random copolymers (5). In #52, 70% by weight Zytel 61 was mechanically blended on a rubber mill with 30% by weight BCI-1107 (nylon type 11). The resultant blend was placed in an ignition tube under an inert blanked of nitrogen. The temperature was raised to 300°C and maintained for two hours. Number 53 was prepared in similar manner using 75% by weight of Zytel 31 (nylon type 6, 10) and 25% by weight BCI-1107. The resultant copolymers have lower softening points and greater solubility than either of the polymers from which they were prepared. The third polymer, #54, was a commercially available alkylated nylon (800 Series Nylon type 8) with a softening point of about 136°C.

Each nylon was in turn combined with an epoxy resin by standard rubber milling techniques in a manner similar to Metlbond 406. The resulting adhesive compositions were cured 1 hour at 350°F and 25 psi in order to be used for bond preparation.

Table 11 reveals the results of this study. Conclusions drawn from the work were that the softening point of the nylon itself is not a clear-cut method for improving the low temperature strength of a nylon-epoxy adhesive, using Metlbond 406 as control. Although there was a slight tendency to improve the -320°F tee peel strength, the room temperature properties suffered drastically. There was even slighter tendency for lower softening point nylons to improve the -320°F tensile shear strength. Metlbond 406 continued to outperform the experimental adhesives.

IX. STUDY OF MODIFIED NYLONS AS IMPROVED ADHESIVES FOR APPLICATION AT VERY LOW TEMPERATURE

It has been reasoned for some time that a copolymer could result between a nylon type polymer and an epoxy function by virtue of the nucleophillic character of the nitrogen links of the nylon polymer. For example, it has been observed that if Zytel 61 (nylon copolymer) is heated in the presence of an epoxy resin (Epon 828) at 500°F for 1 hour, the properties of the nylon are substantially changed (i.e., it becomes insoluble and infusible). In general, however, the conventional glycidyl ether type epoxy resins are not mutually compatible with nylon, per se; therefore, mechanical blending or mixed solvent systems must be used to effect some degree of a homogeneous dispersion.

TABLE 11

A STUDY OF NYLON POLYMER AND COPOLYMER CHEMICAL STRUCTURE TO OPTIMIZE ADHESIVE STRENGTH AT EXTREMELY LOW TEMPERATURE

Metlbond 406 Type Formulations

Code No.	Nylon Composition	Nylon Softening Point, °C	Nylon-Epoxy Adhesive Strength			
			Tensile Shear, psi*		Tee Peel, lbs/1"**	
			R.T.	-320°F	R.T.	-320°F
METLBOND 406 (Control)		138	5470+	4840	--	8.33
18	See Table 10	138	4812	2718	7.5	3.0
48	See Table 10	30	5670	3285	10.0	5.0
52	Zytel 61 70% BCI-1107 30%	121	4390	3715	20.0	10.0
53	Zytel 31 75% BCI-1107 25%	162	4440	5022	6.0	10.0
54	BCI-3218	136 (Approx.)	2112	1776	100.0	2.5

* Cure: 1 hour at 350°F and 25 psi. Average of 4 specimens.

** Single specimens.

Naturally, the thought occurred of using low molecular weight oxirane mono-
mers to overcome the respective mutual insolubility. Preliminary work in this area
was fairly successful. On treating Zytel 61 with 1) butadiene diepoxide and with
2) resorcinol diglycidyl ether, polymeric materials were obtained with melting
points noticeably lower and solubilities appreciably greater than the parent
nylon.

Upon heating 1) or 2) at approximately 350°F for one hour, the molecular
weight was noted to increase so markedly that a fair degree of room temperature
rigidity was apparent. Upon subjecting the untreated Zytel 61 to Kjeldahl
nitrogen analysis, a 10.5% level was obtained. Analysis of the butadiene
diepoxide and nylon copolymer showed a 7.5% level, or a drop of 2.5%. This
strongly suggested grafting (6) of alkoxy groups onto a great many of the amide
groups throughout the nylon chain, for if only end groups were reacting, the
percentage decrease of nitrogen would be essentially negligible in a high
molecular weight polymer such as Zytel 61. On the basis of this reasoning, it is
not surprising that additional increase in molecular weight occurs as the other
oxirane group of the difunctional monomers further reacts with other amide
groups as the temperature is increased -- the net result being some degree of
crosslinking.

Althrough the ratios of reactants in the above-mentioned study are arbitrary,
it appeared that the oxirane function was present in a more than ample amount as
evidenced by the "salting out" of the polymer upon treatment of the reaction
mixture with a solvent for the monomer (methyl ethyl ketone).

It was hoped that this initial study would lead to a technique for improving
the very low temperature properties of nylon by offering a control over
crystallinity, crosslinking, and general polymer configuration.

Table 12 shows the results of the initial attempts to use these graft poly-
mers as 1-part thermosetting nylon adhesives. The initial data are quite interest-
ing.

Included in the above study was the alkylation of the same nylon copolymer,
Zytel 61, by refluxing an alcoholic solution for 8 hours in the presence of
excess paraformaldehyde. Similar techniques are employed for alkylation of nylon
type 6,6 for producing nylon type 8 which can be crosslinked with heat in the
presence of anhydrides and trace quantities of amide. The results here were not
very rewarding.

Table 13 lists some molecular weights and percent nitrogen for various nylons.
The molecular weight determination was accomplished by freezing point depression
in phenol. Generally, the freezing point depression constant K_f for phenol is ex-
pressed as an analytical function of its normal freezing point and latent heat of
fusion, and gives a value of — 7.4 °C/mole solute. However, for nylon type
solutions in phenol, this constant does not hold and K_f must be determined by
using a solute of known molecular weight. From the expression:

TABLE 12

INITIAL STUDY OF MODIFIED NYLONS AS IMPROVED ADHESIVES
FOR APPLICATION AT VERY LOW TEMPERATURE

Modification of Nylon	Tensile Shear,*psi		Tee Peel,** lbs/1"	
	RT	-320°F	RT	-320°F
1. Alkylation An alcoholic solution of Zytel 61 was refluxed for 8 hours in the presence of excess para-formaldehyde	The resultant polymer was alcohol insoluble. No further work was done.			
2. Alkoxylation Ten grams of Zytel 61 were heated in 100 grams of Epon 828 epoxy resin with good agitation for 3 hours at 500°F	The resultant polymer was a deep amber color and found to be alcohol insoluble and infusible. No further work was done			
3. Alkoxylation Ten grams of powdered Zytel 61 were heated in 100 grams of Epon 828 epoxy resin with good agitation for 48 hours	The resultant polymer was alcohol insoluble. No further work was done			
4. Alkoxylation Equal parts by weight of powdered Zytel 61 and butadiene diepoxide were refluxed for 2 hours	Resultant polymer was thermosetting			
	1082	1408	7.5	5.0
5. Alkoxylation Equal parts by weight of powdered Zytel 61 and resorcinol diglycidyl ether were refluxed for 2 hours	Resultant polymer was thermosetting			
	598***	3660***	5.0***	15.0***

*   Average of four specimens

**   Single specimens

***   Polymer was employed for bonding a Na-naphthalene treated Teflon FEP sub-strate

TABLE 13

PROPERTIES OF VARIOUS NYLONS

Nylon Designation of Composition	Molecular Weight	% Nylon	Softening Point, °C*	Preparation Procedure
Zytel 61	6,100	10.6	140	---
Type 11; (Polylactam of 11 amino undecanoic acid)	11,000	--	182	---
Type 11 + Type 6,10 2:1	18,500	--	165	Reaction 300°C 2 hrs - under dry N_2
Type 6,10	17,000**	--	220	---
Type 6	---	--	210	---
Type 6/Type 6,10 75/25	---	--	200	Reaction 300°C 2 hrs - under dry N_2
Type 6/Type 6,10 50/50	---	--	190	"
Type 11/Zytel 61 25/75	---	--	160	"
Type 6/Type 11 35/65	---	--	186	"
Type 6/Type 7/Type 11 1/1/1	---	--	110	"

   * Softening points determined by parallel plate plastometry previously described

 ** Literature values

Materials Identification

  Zytel 61 nylon copolymer - Dupont
  Type 11 nylon - BCI #1107
  Type 6,10 nylon - Zytel 31
  Type 6 nylon - Plaskon #8200P

$$K_f = \frac{G\,M\,\Theta_f}{1,000\,g}$$

G = Weight of phenol
g = Weight of nylon solute
Θ_f = Observed freezing point depression
M = Mole weight

using two nylons of known molecular weight (i.e., a type 6,10 of molecular weight = 17,000, and a type 6,6 of molecular weight = 18,000), an average value for K_f = 150.0 was obtained. Using this value of K_f, the molecular weights of Zytel 61, a standard type 11 nylon and a type 6,10-11 graft polymer were obtained.

It will be recalled that upon reaction of Zytel 61 with butadiene dioxide, a copolymer was obtained which gave an average nitrogen composition of 7.7% (by Kjeldahl), as compared to pure Zytel 61 which is 10.6% nitrogen. Assuming that one mole of BDO was equivalent to two equivalents of N-H (the number of N-H sites being calculable from the now known molecular weight and previously determined percent nitrogen of Zytel 61), a calculated nitrogen content of 7.9% was obtained. Thus, it would appear that this 2/1 equivalency between N-H and diepoxide monomer, on the average, seems to hold. This relationship, on the basis of total Zytel 61 molecule, comes out in a molar ration of $\simeq$ 23:1 (i.e., BDO:Zytel 61) and therefore would be expected to hold for other diepoxides as well.

A study using various other diepoxide compounds with various other nylons was instituted. In general, nylons were selected (as was done earlier) on the basis of low melting point (i.e., 160°C or lower). Table 14 gives a list of compositions and softening points for the various nylons used. An additional diepoxide compound has been used to date: bisphenol "A" diglycidyl ether (DER 332). RDGE and BDO were sufficiently reactive so that certain of the nylon compositions were seen to react directly with them, by evidence of solution at $\simeq$ 1000°C. On the other hand, DER 332 was not as reactive; a mutual solvent must be employed (e.g., N-methyl-2-pyrrolidone) to effect initial homogeneity, which seems to be necessary for a satisfactory reaction.

Table 14 also shows RT and -320°F tensile shear and tee peel data for some various copolymer compositions. Some of these employed the straight solution cast polymer applied to the metal, using a shimmed glueline. Others employed a substrate reinforcing film. These are given the Greek letter designation Epsilon (ε) through Kappa (κ) for the description of resin systems. The data for these nylon-epoxy systems are, of course, average numbers and therefore reflect a somewhat notable scatter in data obtained thus far. Initially, the through Eta (η) copolymers were applied from solution, and thus build-up was difficult. The latest ι and κ were employed as precast films in correct thickness to improve consistency of the glueline. In formulation, the addition of dicyandiamide appears to improve the nylon-epoxy copolymer, possibly through crosslinking at residual epoxy sites.

With this in mind, formulation Lambda (λ), Nu (ν), Xi (ξ), and Pi (π) employed varying amounts of dicyandiamide and methylene dianiline (MDA). In all cases, however, inspection of gluelines after failure showed the material to be rather gummy. That freezing to a more rigid state occurred at -320°F is reflected in a majority of cases by a rise in tensile shear strength (Table 14).

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TABLE 14

TENSILE SHEAR AND TEE PEEL DATA FOR VARIOUS NYLON-EPOXY ADHESIVES

Resin Desig.	Cure	Resin Preparation and Properties	Tensile Shear,* psi R.T.	Tensile Shear,* psi -320°F	Tee Peel,**lbs/1" R.T.	Tee Peel,**lbs/1" -320°F
Epsilon ε	1 hour 350°F cure shim glueline .004"	BDO***-100 pts; Zytel 61-20 pts (25/75) reacted at 160°C under dry N₂ for 2 hours. Precipitated and purified from pot residue; flow point ≅ 250°F. Alcohol soluble	1634	1020	10.0	0.5
Epsilon₂ ε	1 hour 350°F cure Na-Naph. etched FEP substrate .004"	"	1082	1408	7.5	5.0
Zeta₂ ζ	1 hour 350°F cure, Na-Naph. etched Kel-F substrate .004"	RDGE-100 pts; Zytel 61-20 pts (25/75)-reacted at 160°C under dry N₂ for 2 hours. Precipitated and purified from pot residue; flow point ≅ 250°F. Alcohol soluble	598	3660	5.0	15.0
Zeta ζ	"	"	3128	1416	5.0	5.0
Eta η	1 hour 350°F cure shim glueline .004"	RDGE-100 pts; Type 11/Zytel 61 (25/75)-20 pts. Reacted at 160°C under dry N₂ for 2 hours. Precipitated and purified from pot residue; flow point ≅ 250°F. Alcohol soluble	2180	1468	12.5	2.5
Eta₂ η	1 hour 350°F cure .004" Na-Naph. Etched Kel-F substrate	"	1638*	****3075	12.5	17.5
Iota ι	1 hour 350°C cure .004" shim glueline, solution precast film	DER 332-100 pts; Nylon 11/61(25/75) 40 pts. Reacted in N,methyl-2-pyrolidone; 140 mls for 2 hrs @ 160°C. Precipitated and purified from pot; flow point ≅250°F. Alcohol soluble	2982	1588	*****9.0	1.0
Kappa κ	1 hour 350°C cure .001" glueline, no shin; precast solution film	Same as iota, except mixed in alcohol with dicyandiamide (15 phr) solids	1920	2490	--	--

TABLE 14 (Continued)

Resin Desig.	Cure	Resin Preparation and Properties	Tensile Shear,* psi R.T.	Tensile Shear,* psi -320°F	Tee Peel,**lbs/1" R.T.	Tee Peel,**lbs/1" -320°F
Lamda λ	1 hour 350°F cure .001" glueline, no shim; precast solution film	DER 332-100 pts; Nylon6/7/11(1/1.1) ~40 pts. Reacted in N,methyl-2-pyrolidone; 140 mls for 2 hours @ 160°C.	1441	853	5.0	0.5
Nu ν	Same as Lamda	Same as Lamda except 10 phr dicyandiamide	2395	1293	2.5	1.0
Xi ξ	1 hour 250°F cure .004" glueline solution precast film	Same as Iota, except added 16 phr Mda	724	1206	5.0	2.0
Xi ξ3	Same except no .004" shims	"	1215	1873	---	---
Xi ξ4	Same except used .004" shims	Same as Iota except 8 phr MDA	1151	1631	---	---
Xi ξ5	"	Same as Iota except 45 phr MDA	Not suitable for testing			
Pi π	"	Same as Iota except DER 331 and 16 phr MDA	715	1414	7.5	1.5
Pi π2	Etched Kel-F film (.005" substrate)	"	819	2020	2.0	10.0

* Average of four specimens
** Single specimens
*** Butadiene dioxide
**** Skewed glueline
***** Damaged specimen

All bonding pressures were at 25 psi. Four mil aluminum shim wires were used to control glueline thickness

It was concluded that the use of crosslinking agents, such as MDA, does effect the mechanical properties of the nylon epoxy copolymer, but not sufficiently enough to produce desirable rigidity. The incorporation of additional epoxy function in the copolymer greatly increases rigidity, but appears to reduce toughness.

X. NEW NYLON-EPOXY AND POLYAMIDE-EPOXY POLYMERS FOR EVALUATION AS ADHESIVES, OR ADHESIVE CONSTITUENTS, AT VERY LOW TEMPERATURE

A. Nylon-Epoxy Graft Polymers Based on the Solvating Action of N-Methyl-2 Pyrollidone

In a resin flask equipped with stirrer, thermometer, and heating mantle were placed 80.0 grams of a comparatively low molecular weight aliphatic epoxy resin (Epon 812) and 20.0 grams of a finely divided nylon copolymer (Zytel 61). The reactants were heated at 130°C for 4-1/2 hours, followed by cooling to ambient temperature. The mixture was found to be heterogeneous, containing undissolved globules of nylon in the epoxy matrix. The mixture was filtered, and the residue washed free of epoxy resin with methyl ethyl ketone and dried. The infrared spectra of the residue failed to reveal absorbance in the epoxide regions (approx. 8 and 11 microns) which would prove epoxy grafts on the amide groups of the nylon. In addition, because the residue was a high molecular weight, high melting solid, it was considered unsuitable for an adhesive intended for processing at ambient temperature.

In a resin flask equipped with stirrer, thermometer, heating mantle, and condenser were placed 160.0 grams of an aliphatic epoxy resin (Epon 812), 40.0 grams of a finely divided nylon copolymer (Zytel 61) and 160.0 grams of N-methyl-2-pyrrolidone solvating agent. The reactants were heated at 130°C for 4-1/2 hours, after which a clear, homogeneous solution resulted. Cooling to ambient temperature resulted in gellation of the reaction mixture. The mixture was washed free of pyrrolidone with water and washed free of epoxy resin with methyl ethyl ketone, leaving a rubbery residue found to be insoluble in the epoxy resin starting material (Epon 812). An infrared spectra of the residue revealed appreciable absorbance in the epoxide regions, indicating that epoxy grafts on the nylon had been attained by the solvating action of the pyrrolidone. Again, because the residue was of higher molecular weight (than the nylon starting material, due to grafting), it was considered unsuitable for an adhesive intended for processing at ambient conditions.

B. Nylon-Epoxy Graft Polymers Based on the Reaction of Nylon with Epoxy Monomers

In a resin flask equipped with stirrer, thermometer, heating mantle, and condenser were placed 100.0 grams of resorcinol diglycidyl ether (diepoxide monomer) and 20.0 grams of a finely-divided nylon copolymer (Zytel 61). The reactants were heated at 150°C until the mixture had gained homogeneity as evidenced by clarity. The reaction product was cooled to ambient, and washed free of monomer with methyl ethyl ketone. The residue resembled the nylon starting material and showed a strong infrared absorbance in the epoxide regions. It was concluded that grafting had indeed taken place, but the solid, high molecular weight nature of the material precluded an adhesive which could be processed at ambient conditions.

C. Compatibility of Type 8 Nylon with an Epoxy Resin

Based on previous experience, it is known that at least 25 and preferably 75 weight percent of a suitable nylon is required for modification of an epoxy resin intended as an adhesive for very low-temperature application. At the 25% level the nylon may be satisfactorily employed at ambient conditions as a filler; nevertheless, at the 75% level, elevated temperature fusion of the nylon is required for adhesion.

The compatibility of nylon type 8 (BCI 819), a N-methylated nylon, was studied in a low viscosity epoxy aliphatic resin (Epon 812). The purpose was to incorporate the maximum nylon in the resin and still have at least a semi-solid which could be processed at room temperature by curing with a reactive polyamide resin. It was found that 15 weight percent of nylon 8 was compatible, but that the viscosity was almost too high for ambient temperature processing. The low nylon level and the high viscosity precluded a practical adhesive.

XI. STUDY OF FILLERS FOR ADHESIVE BONDING AT EXTREMELY LOW TEMPERATURE

The use of fillers in certain structural adhesives is common practice. Fillers are generally added to accomplish some specific purpose or to assist in eliminating some shortcoming in the base resins. Fillers may provide viscosity and flow control, change in coefficient of thermal expansion, change in heat conductivity, change in extensibility, and effect on similar characteristics. In the case of low-temperature adhesives, fillers serve best as a means of altering the coefficient of expansion of the cured systems.

Fillers were selected on the basis of their coefficient of thermal expansion: Zytel 61 (nylon) for high coefficient, higher than adherend; Alcoa 123 (aluminum) for comparatively low coefficient, approximating that of the adherend; and silica and alumina for low coefficient, lower than adherend.

The resin selected was Resin 3135, an epoxy polyamine system. This unfilled adhesive was selected because it very closely resembles the adhesive desired by the National Aeronautics and Space Administration in this work; namely, ease of surface preparation and bonding procedures.

. The fillers were used at 33.3, 66.7, and 100 parts per 100 parts of Resin 3135. The total amount of filler was divided in half; one-half being stirred into the epoxy component of the resin and the other half being stirred into the polyamine component. This was done to assure complete wettability of the filler before combining the two reactive portions of the resin.

The two filled portions of Resin 3135 were then combined and used to coat (with spatula) the faying surfaces of 7075T6 bare aluminum breakaway panels. The bonds were assembled with 1/2" overlap by means of curing fixtures, and cured 48 hours at RT and contact pressure. The bonds were subsequently tested in tensile shear at RT and $-320°F$. Data are shown in Table 15 and Figures 18 and 19.

TABLE 15

STUDY OF FILLERS FOR ADHESIVE
BONDING AT EXTREMELY LOW TEMPERATURES

Filler, Parts by Weight per 100 Parts Resin 3135	Adhesive Coefficient of Linear Thermal Expansion (-320 to +32°F) in/in/°F x 10⁵	Tensile Shear Strength, psi*	
		R.T.	-320°F
0, CONTROL	3.21	2682	1514

Nylon (Zytel 61),
(<200 mesh),
   33.3 (ADHESIVE A)
   66.7
   100.0
	
	3.17
	3.15
	3.18
		
		3140
		2150
		1970
			
			3180
			2895
			2307

Aluminum (Alcoa 123)
(18 micron average),
   33.3
   66.7
   100.0
	
	2.72
	2.50
	2.21
		
		3400
		3230
		2610
			
			1877
			2672
			2960

Silicon Dioxide
(Quartz, <200 mesh),
   33.3
   66.7
   100.0
	
	2.69
	2.10
	1.87
		
		2530
		2720
		2480
			
			1570
			1782
			2130

Alumina
(<200 mesh),
   33.3
   66.7
   100.0
	
	2.44
	2.23
	1.88
		
		2900
		2650
		2830
			
			1935
			1982
			1935

Curing cycle: 48 hours at R.T. and contact pressure.

* Average of 8 specimens each.
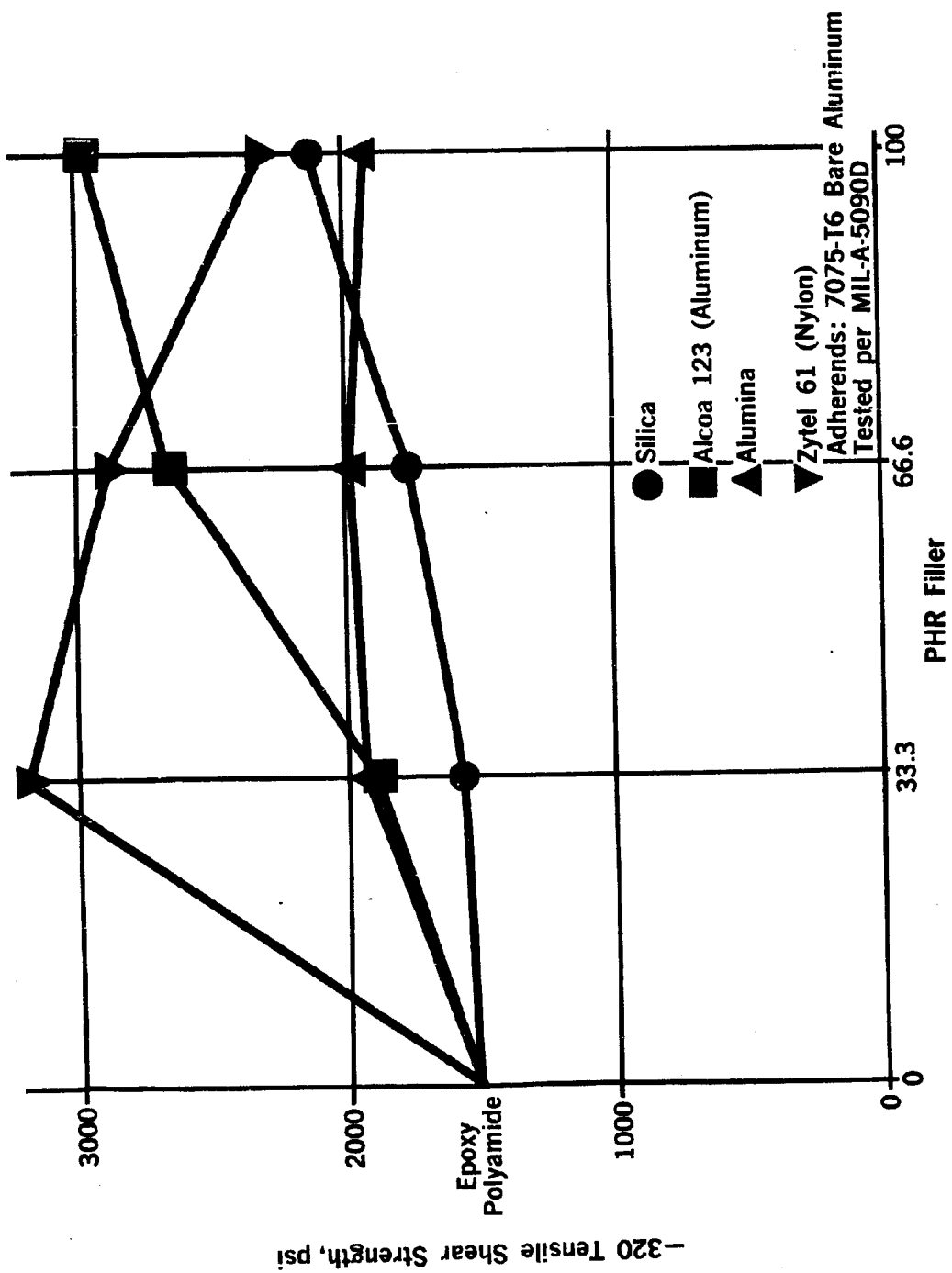
Figure 18. The effect of various fillers and loadings on the -320°F strength of Resin 3135
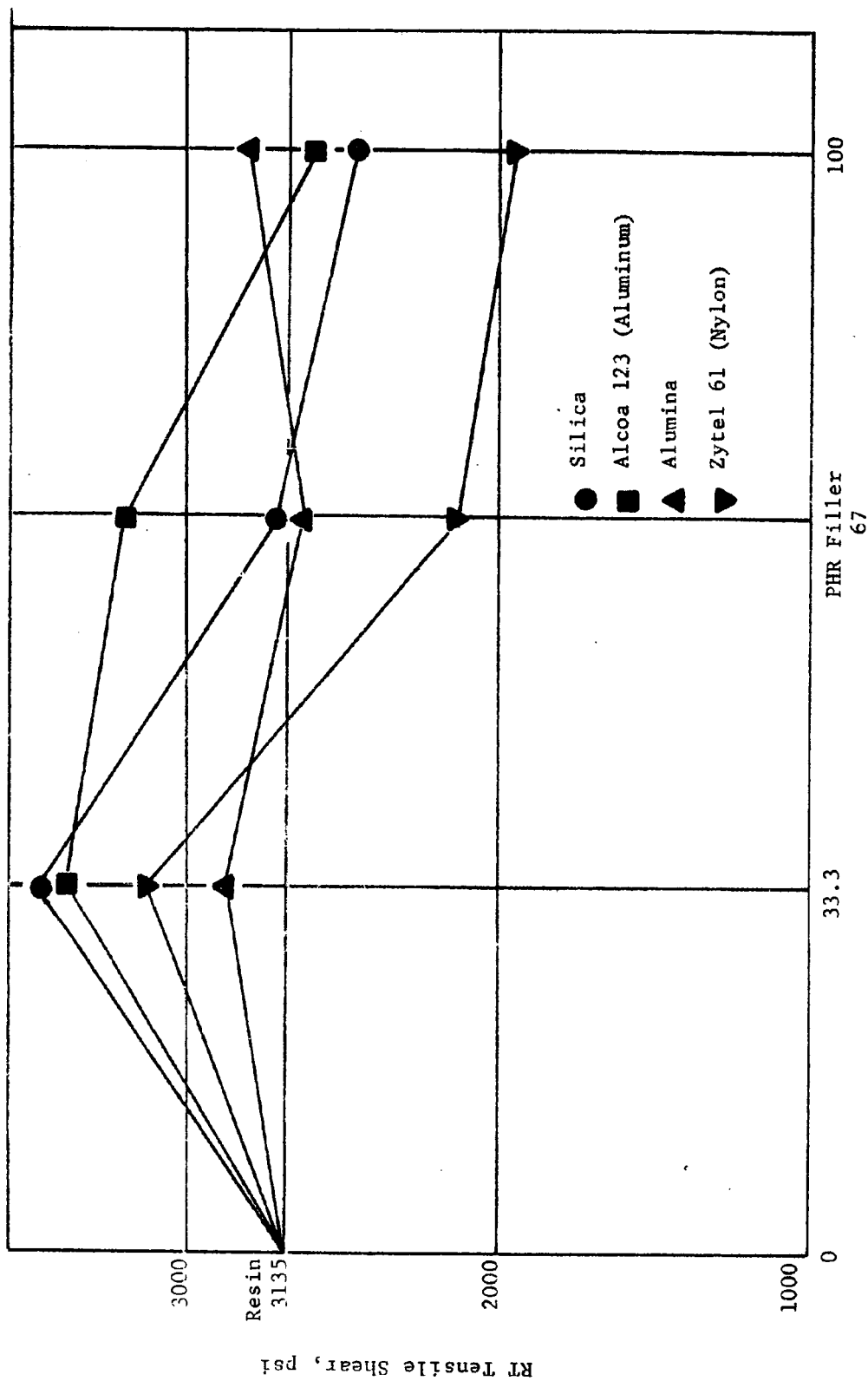
Figure 19. The effect of various fillers and loadings on the RT strength of Resin 3135 bonds

Coefficient of thermal expansion specimens were prepared at the same time by casting each filled Resin 3135 sample in 0.4" ID x about 2" long polyethylene tubing. Specimens were cured 48 hours at RT before testing over the temperature range -320 to +32°F. Test procedures were those described previously, except that a change to copper-Constantan thermocouples was made to improve reliability (7). In addition, a multiple-junction "thermal" (8) or thermopile was employed. Data are shown in Table 15 and Figure 20.

It was concluded from this filler study that the type of filler was probably more important to adhesive strength at low temperature than the thermal contraction of the specific filler. All fillers improved the low-temperature strength of Resin 3135; however, nylon (Zytel 61) appeared to be far superior. Peel strength is shown in Table 16, Code #151 and Control.

Because of the promising results obtained from fillers in the foregoing work, additional studies were conducted. Polymeric fillers(such as nylon, polyester, polyvinyl alcohol, polyvinylidene fluoride and chloride, polytetrafluoroethylene, polycarbonate, etc.) and metallic fillers(such as copper and lead, which exhibit good ductility at low temperature)were evaluated with Resin 3135. The polyamide-to-epoxy-weight ratio for Resin 3135 was changed from 50/50 to 67/33 as suggested by the studies in subsequent Section XII. All fillers were employed at a loading rate of 33.3 parts per hundred parts of resin; cure was accomplished at room temperature and contact pressure. Table 16 shows the results of this work. Although none of the fillers performed as well as nylon in tensile shear over the temperature range from -320°F to RT, it was interesting to note that many demonstrated better properties at -320°F than at RT. Improvements were noted in tee peel, both at -320°F and RT. Increasing the polyamide content of Resin 3135 and using nylon filler did not result in the improvements expected.

It was decided to study the effects of discrete nylon fibers as fillers. It was anticipated that a fiber could contribute better reinforcing effects than a small particle. A nylon fabric material and a nylon felt material were obtained and macerated by passing through the nip of a typical rubber mill. The result was reduction of the material to short, individual nylon fibers. These were used at various loading rates to fill Resin 3135/7111 and to compare with data collected for Adhesive A. Table 16 (Code #200, 201, 202, and 205) shows the results of this study. In general, the tensile shear and tee peel are quite comparable with Adhesive A, and no outstanding advantages are seen for fiber fillers.

Resin 3147/7125 was used to replace the resin and curing agent in Adhesive A, which subsequently was filled with 33.3 phr, 200-mesh, Zytel 61 nylon powder. As shown in Table 16 (Code #209), there was a slight increase in RT tensile shear strength. In general, no particular advantages could be seen for this replacement.

It was further decided to study the effect of nylon filler in a polyurethane elastomer adhesive. Two-hundred-mesh powdered Zytel 61 nylon, at a loading rate of 33.3 phr, was incorporated in the elastomer. Specimens were prepared by curing at RT and contact pressure. Table 16 (Code #271) shows the results of the study. Nylon filler in a polyurethane elastomer does not, in general, enhance the overall adhesive properties.
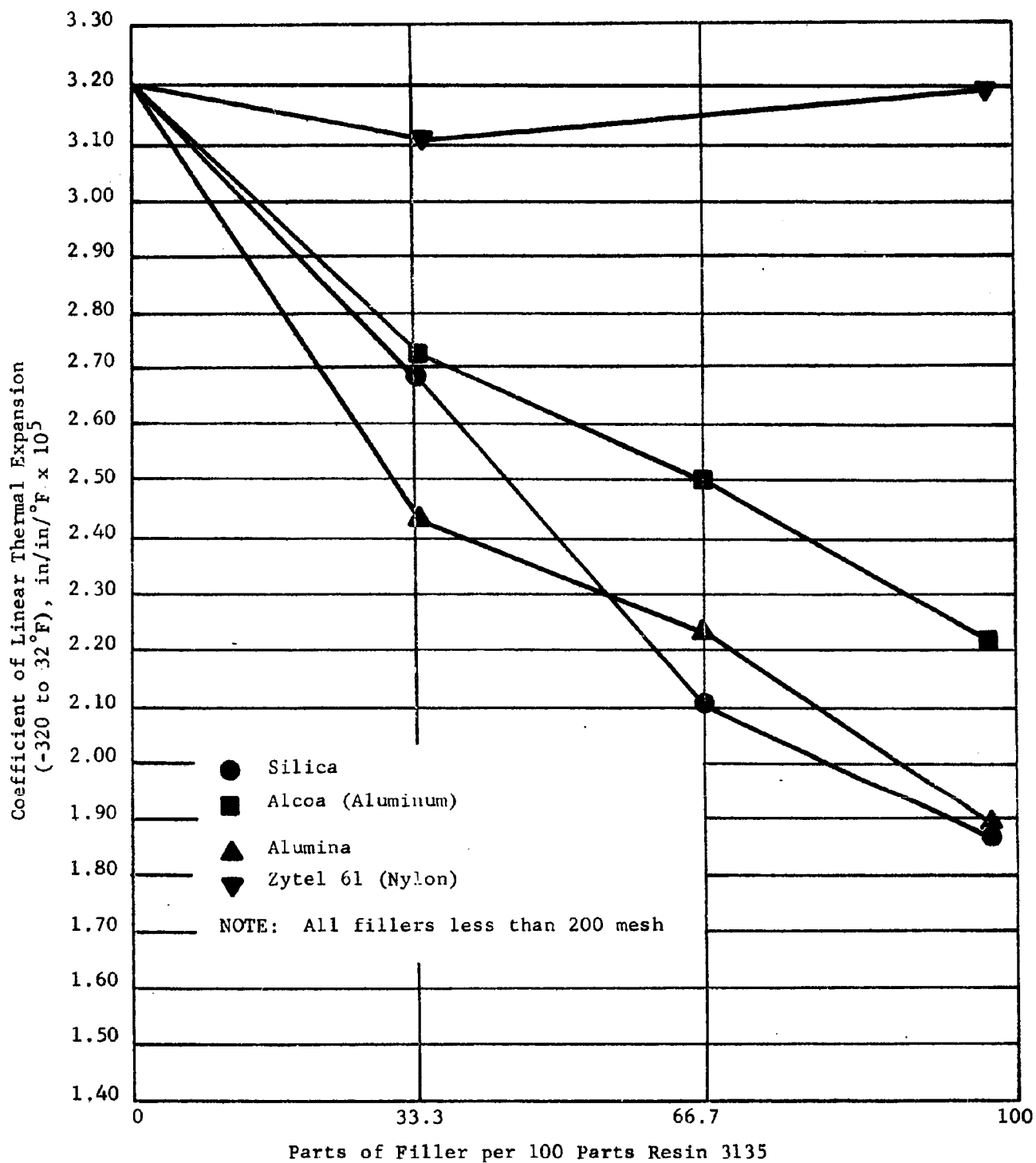
Figure 20. Effect of various fillers and loadings on the coefficient of linear thermal expansion of Resin 3135

TABLE 16

CONTINUED STUDY OF FILLERS FOR ADHESIVE BONDING
AT EXTREMELY LOW TEMPERATURE

Code	Adhesive System	Weight Ratio, Polyamide to Epoxy	Cure	Tensile Shear,* psi		Tee Peel,** lbs/1"	
				R.T.	-320°F	R.T.	-320°F
POLYMERIC FILLERS							
PVA	Resin 3135, 33.3 phr Elvanol (200 mesh) polyvinyl alcohol	50/50	8 Days at RT	3480	1440	3.0	2.5
KYNAR	Resin 3135, 33.3 phr Kynar (200 mesh) vinylidine Fluoride	50/50	8 Days at RT	2710	2947	2.5	2.5
MYLAR	Resin 3135, 33.3 phr Mylar (100 mesh) polyethyleneterephthalate	50/50	8 Days at RT	2875	1892	7.5	6.0
C	Resin 3135, 33.3 phr Teflon 7 (200 mesh) polytetrafluoroethylene	50/50	7 Days at RT	2782	2895	6.0	4.0
E_1	Resin 3135, 33.3 phr Teflon 7 (200 mesh) treated with Na-amide, polytetrafluoroethylene	50/50	8 Days at RT	3170	2672	7.5	5.0
G	Resin 3135, 33.3 phr Saran 723 (200 mesh) polyvinylidene chloride	50/50	8 Days at RT	3195	2492	3.5	4.0
I	Resin 3135, 33.3 phr Delrin (200 mesh) acetal	50/50	6 Days at RT	2835	2032	5.0	5.0
K	Resin 3135, 33.3 phr Lexan (200 mesh) polycarbonate	50/50	6 Days at RT	2810	1399	5.0	3.5
CON-TROL	Resin 3135, 33.3 phr Zytel 61 (200 mesh) nylon Adhesive A	50/50	2 Days at RT	3140	3180	2.0	2.5
151	Resin 3135, 33.3 phr Zytel 61 (200 mesh) nylon	67/33	11 Days at RT	2310	2760	5.0	2.5
BC	Resin 3135, 33.3 phr polypropylene (200 mesh)	50/50	1 Hour at 250°F	2212	1804	5.0	5.0
AS	Caprolactone-propylene oxide and TP-440, 33.3 phr Teflon 7 (200 mesh) polytetrafluoroethylene	--	1 Hour at 250°F	1620	4047	40.0	15.0
AT	Same as "AS", except 20 phr Teflon-7 (200 mesh) polytetrafluoroethylene	--	1 Hour at 250°F	1503	4687	22.5	10.0

TABLE 16 (Continued)

Code	Adhesive System	Weight Ratio, Polyamide to Epoxy	Cure	Tensile Shear,* psi		Tee Peel,** lbs/1"	
				R.T.	-320°F	R.T.	-320°F
METALLIC AND INORGANIC FILLERS							
100	Resin 3135, 33.3 phr copper (200 mesh)	50/50	6 Days at RT	3970	1326	5.0	2.5
101	Resin 3135, 33.3 phr lead (200 mesh)	50/50	6 Days at RT	3485	1409	2.5	4.0
154	Resin 3135, 33.3 phr lead (200 mesh)	67/33	5 Days at RT	1742	1594	15.0	2.5
155	Resin 3135, 66.7 phr lead (200 mesh)	67/33	5 Days at RT	3080	2067	12.5	3.0
156	Resin 3135, 100 phr lead (200 mesh)	67/33	5 Days at RT	2479	2295	15.0	3.5
---	Resin 3135, 25 phr zinc oxide (200 mesh)	50/50	1 Hour @250°F	3790	1595	2.5	1.5
200	Resin 3135/7111 + 33.3 phr macerated nylon marquisette fibers	--	9 Days at RT	2150	2595	2.75	3.75
201	Same as #200, except 22 phr	--	8 Days at RT	2802	2520	2.0	3.3
202	Same as #200, except 11 phr	--	8 Days at RT	3037	2152	3.0	5.0
205	Resin 3135/7111 + 11 phr macerated Ny-Sul-Loft 1370 nylon felt fibers	--	8 Days at RT	3557	1825	5.5	7.0
209	Resin 3147/7125 + 33.3 phr 200 mesh Zytel 61 nylon powder	--	7 Days at RT	3595	2718	4.5	4.0
271	Adiprene L-100 + 11 phr Moca + 33.3 phr 200 mesh Zytel 61 nylon powder	--	8 Days at RT	667	5225	9.0	11.0
E_2	Resin 3135/7111 + 33.3 phr Teflon 7 etched with Na-naphthalene	--	3 Days at RT	2130	2035	5.0	3.5
307	Commercial etched Teflon TFE Powder at 33.3 phr with Resin 3135/7111	--	11 Days at RT	2195	1692	6.1	4.1
309	ADHESIVE C plus 33.3 phr Teflon 7 200 mesh powder	--	3 Days at RT	1347	4770*	19.7	16.5
310	Same as #309, except 67.7 phr Teflon 7	--	3 Days at RT	1007	4125	15.7	7.0

TABLE 16 (Continued)

Code	Adhesive System	Weight Ratio, Polyamide to Epoxy	Cure	Tensile Shear,* psi		Tee Peel,** lbs/1"	
				R.T.	-320°F	R.T.	-320°F
311	Same as #309, except 100 phr Teflon 7	--	3 Days at RT	1122	4492	11.5	11.3
312	ADHESIVE D plus 33.3 phr Teflon 7 200 mesh powder	--	3 Days at RT	1729	5205*	17.6	20.5
313	Same as #312, except 67.7 phr Teflon 7	--	3 Days at RT	1505	4250	14.5	5.5
314	Same as #312, except 100 phr Teflon 7	--	3 Days at RT	1610	4635	9.1	7.5

* Average of 4 specimens

** Single specimens

Two-hundred-mesh Teflon 7 was etched in the standard sodium naphthalene solution and subsequently used to fill the epoxy-polyamide Resin 3135/7111 adhesive at a loading rate of 33.3 phr. The results (shown in Table 16) were not as good as those where the Teflon was etched with sodium amide.

To add to the filler studies already conducted, a commercially etched Teflon TFE powder was obtained and used to fill the epoxy polyamide adhesive (Resin 3135/7111) at a loading rate of 33.3 phr. Table 16 shows the data generated. This filler did not appear as promising as other grades of Teflon, using adhesive strength and toughness as test criteria.

Polyurethane elastomers (see Section XV) were also filled with 33.3, 67.7 and 100 phr of unetched Teflon 7 filler. The filler did not improve the tensile shear or tee peel strengths of these adhesives, either at ambient or cryogenic temperatures.

A. Selection of Adhesive A

The adhesive consisting of 33.3 phr powdered nylon in an epoxy polyamide resin, cured at RT and contact pressure (referred to above and noted in Tables 15 and 16 and Figures 17, 18 and 19), was selected for further evaluation and study in view of its ease of processability, excellent moderately low-temperature strength properties, and fair strength and toughness at low temperature. This system was designated as Adhesive A and later designated as Narmco Resin 3170 and Curing Agent 7133.

XII. A STUDY OF ROOM-TEMPERATURE-CURED EPOXY POLYAMINE ADHESIVE SYSTEMS FOR APPLICATION AT VERY LOW TEMPERATURE

A. Weight Ratios of Epoxy to Polyamide Constituents

Until now the room-temperature-curing Resin 3135 epoxy-polyamide system was employed with only the manufacturer's recommended weight ratio of polyamine to epoxy constituents; namely, 50/50. Obviously, there was no way of knowing whether the stoichimetry was optimum over the temperature ranges of interest here. It was also appreciated that other ratios and other epoxy and polyamine resins with greater and lesser epoxide and amine equivalents, respectively, might offer advantages over the Resin 3135 system. It was also desired to know the low temperature properties of epoxy resins cured at room temperature with amines.

The polyamine and epoxy constituents of Resin 3135 were first combined in the following weight ratios: 33/67, 50/50, and 67/33, respectively. Tensile shear specimens were prepared with the resultant mixes by curing at room temperature and contact pressure, using 4-mil aluminum shim wires to control glueline thickness. A series of other polyamine and epoxy resins, considered worthy of evaluation, were then treated in identical manner. Finally, four different amine curing agents were evaluated against one epoxy resin.

Table 17 shows the results of this work. Resin 3135 was found to be the superior epoxy-polyamine adhesive system. Although a polyamide/epoxy weight ratio of 67/33 gave better low-temperature strengths than the 50/50 ratio, this fact was not evident when used with nylon filler (see Section XI). The polyamine to epoxy weight ratio was accordingly maintained at 50/50. The adhesive strengths of epoxy resins cured with amines were far inferior to the epoxy-polyamines.

B. Synthesis of New Polyamide Polymers

It was anticipated that improved adhesive performance at very low temperature could result from new polyamides and/or nylons, particularly if the polyamides or nylons were amine terminated for subsequent crosslinking with epoxy resins, and if the polyamides or nylons were formed from unusually long chain dibasic acids and/or diamines.

1. In a resin flask equipped with stirrer, thermometer, and heating mantle were placed 98.7 grams of Empol 1024 (consisting of 75% of a C_{36} dibasic acid and 25% of a C_{54} tribasic acid). To this were added (dropwise, with good stirring) 11.0 grams (10% excess) of ethylene diamine at ambient temperature. After completion of the addition, the temperature was raised to 120°C for one hour while passing a stream of nitrogen gas over the reactants to entrain and remove water of polymerization. The reaction mixture was then quickly cast and cooled to ambient temperature. A small portion of the reaction mixture was combined with an equivalent weight of an epoxy resin (Epon 828) and heated to 250°F. The admixture could not be thermoset, indicating that the terminal amine groups were not capable of copolymerizing with the epoxy. This was probably due to steric hindrance, incorrect stoichiometry, or the poor compatibility the polyamide showed for the epoxy. The polyamide was not considered promising for further evaluation.

2. In a resin flask equipped with stirrer, thermometer, and heating mantle were placed 98.7 grams of Empol 1014 (consisting of 95% C_{36} dibasic acid, 4% C_{54} tribasic acid, and 1% monobasic acid). To this were added (dropwise, with good stirring) 12.6 grams (10% excess) of diethylene triamine at ambient temperature. After completion of the addition, the temperature was raised to 120°C for one hour while passing a stream of dried nitrogen gas over the reactants to entrain and remove water of polymerization. The reaction mixture was then quickly cast and cooled to ambient temperature. A small portion of the reaction mixture was combined with an equivalent weight of an epoxy resin (Epon 828) and heated to 250°F. The admixture could not be thermoset, indicating that the terminal amine groups were not capable of copolymerizing with the epoxy. As before, this was probably due to steric hindrance, incorrect stoichiometry, or the poor compatibility the polyamide showed for the epoxy. The polyamide was not considered worthy of further evaluation.

3. In a resin flask equipped with stirrer, thermometer, and heating mantle were placed 16.5 grams of Empol 1014 and 50.0 grams of Polyetherdiamine L-2000. After blending, the temperature was raised to 120°C, with good stirring for two hours. A stream of nitrogen gas was passed over the reactants to entrain and remove water of polymerization. The temperature was raised to

TABLE 17

STUDY OF ROOM-TEMPERATURE-CURED EPOXY POLYAMIDE
ADHESIVE SYSTEMS FOR APPLICATION AT VERY LOW TEMPERATURE

Code	Resin System	Days Cure at R.T.	Parts of Polyamide or Amine per 100 parts of Epoxy Resin	Weight Ratio Polyamide/Epoxy or Amine Epoxy	Tensile Shear*, psi	
					R.T.	-320°F
108	Resin 3135	14	49.3	33/67	3425	1404
109	" "	14	100	50/50	2334	1567
110	" "	14	202	67/33	3700	1825
111	Versamid 140/Epon 828	8	49.3	33/67	334	666
112	" "	8	100	50/50	2154	1622
113	" "	8	202	67/33	1782	1356
114	Lancast A/Epon 828	13	49.3	33/67	2428	888
115	" "	13	100	50/50	2765	914
116	" "	12	202	67/33	23	58
117	Epi-Cure 855/Epi-Rez 510	13	49.3	33/67	1667	889
118	" "	13	100	50/50	2615	1257
119	" "	13	202	67/33	137	314
120	Pentamid 1/Epon 828	8	49.3	33/67	2632	2042
121	" "	8	100	50/50	2052	1669
122	" "	8	202	67/33	2283	1928
123	Pentamid 2/Epon 828	7	49.3	33/67	1670	1672
124	" "	7	100	50/50	2282	1883
125	" "	7	202	67/33	1900	2292
130A	Versamid 115/Epon 828	7	49.3	33/67	2770	1812
131A	" "	7	100	50/50	2875	1776
132	" "	7	202	67/33	910	1609
167	Versamid 125/Epi Rez 5132	18	49.3	33/67	2136	1720
168	" "	18	100	50/50	563	644
169	" "	18	202	67/33	114	326
170	Versamid 125/Epi Rez 5042	17	49.3	33/67	1851	1506
171	" "	18	100	50/50	3689	1469
172	" "	18	202	67/33	1286	1250
173	Diethylenetriamine/ Epon 828	18	12	12/100	384	410
174	Triethylenetetra-amine/Epon 828	18	14	14/100	851	427
175	Curing Agent T-1/ Epon 828	17	25	25/100	546	410
176	Curing Agent U/ Epon 828	17	30	30/100	2291	590

* Average of 4 specimens

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250°C for an additional three hours, maintaining good stirring and nitrogen stream. The nitrogen was finally withdrawn and a vacuum (5mm Hg) placed on the system for an additional hour. The reaction mixture was finally cast and cooled to ambient temperature. A very viscous polymer was obtained. A small portion of the polyamide was combined with an equivalent weight of an epoxy resin (Epon 828) and heated to 250°F. While the polyamide was compatible with the epoxy, it could not be thermoset, indicating steric hindrance or incorrect stoichiometry. The high molecular weight polyamide was not considered worthy of further evaluation.

C. Modified Epoxy Resins

Because no significant advantage could be gained from the preceding nylon-epoxy and epoxy-polyamide adhesive studies at extremely low temperature, attention was given to a series of proprietary modified epoxy resins. These resins are designated with an "X" followed by three numerals, and are capable of cure or bonding at ambient temperature and contact pressure. Cure can be accomplished with amines and polyamines.

Table 18 gives the formulation particulars and strength data for the 46 systems which were studied. It appeared that these systems were quite sluggish in curing, and that after even 12 days cure time at ambient temperature and contact pressure their strengths were not worth further investigation. No further work was conducted along the lines of these modified epoxy resins cured with polyamines.

D. Commercial Epoxy-Polyamide Adhesive

A newer epoxy polyamide adhesive, Resin 3147/7125, was evaluated over the temperature range from -320 to +180°F for comparison with the Resin 3135/7111 adhesive system. Having a lower viscosity and faster curing time, it was thought the system would offer distinct advantages. The two components of the system were mixed at equal parts by weight.

Table 19 shows the resulting data. The tensile shear strength at -320°F was more than twice that of Resin 3135/7111, and the tee peel strength at low and ambient temperature was appreciably better. The elevated temperature strength was somewhat of an improvement over Resin 3135/7111. The system shows definite promise for low-temperature bonding applications.

E. Acid and Anhydride Cures for Epoxy Resins

It is a well-established fact that acid and anhydride cures will impart a very high degree of toughness to epoxy resins. The big drawback is that such systems require elevated temperature curing conditions. It was thought that suitable catalysis might bring the curing characteristics in line with the objectives of this program. It was also thought that partial epoxy modification with an acid at elevated temperature might be accomplished, followed by final cure with a polyamine at ambient temperature.

TABLE 18

EVALUATION OF MODIFIED EPOXY ADHESIVE SYSTEMS
AT VERY LOW TEMPERATURE

Code	Adhesive System		Contact Pressure Cure at RT, days	Tensile Shear Strength, psi		Tee Peel Strength, lbs/1"	
				R.T.	-320°F	R.T.*	-320°F
211	X-295	100 Parts	11-12	1043	1644		2.5
	Curing Agent 7111	24.6 phr					
212	Same as #211, except	50 phr	"	913	2652		5.0
213	Same as #212, except	101 phr	"	598	1379		4.0
214	X-295	100 Parts	"	640	1142		1.5
	Curing Agent U	20 phr					
215	X-295	100 Parts	"	1476	1884		2.5
	Versamid 140	50 } 24.6 phr					
	N-Methyl Morpholine	10 }					
216	Same as #215, except	50 phr	"	1038	1995		3.0
217	Same as #215, except	101 phr	"	372	1702		2.5
218	X-296	100 Parts	10-11	1228	1667		4.0
	Curing Agent 7111	24.6 phr					
219	Same as #218, except	50 phr	"	1062	1980		4.0
220	Same as #219, except	.01 phr	"	594	1070		2.5
221	X-296	100 Parts	"	1016	1378		2.5
	Curing Agent U	12.5 phr					
222	X-296	100 Parts	"	1522	1934		2.5
	Versamid 140	50 } 30.7 phr					
	N-Methyl Morpholine	10 }					
223	Same as #222, except	62.5 phr	"	501	1418		2.0
224	Same as #222, except	125 phr	"	320	1052		1.5
225	X-297	100 Parts	7-8	1243	1608		3.0
	Curing Agent 7111	41.2 phr					
226	Same as #225, except	83.5 phr	"	1210	1652		3.0
227	Same as #225, except	167 phr	"	552	1180		2.5
228	X-297	100 Parts	"	1925	1461		1.5
	Curing Agent U	20 phr					
229	X-297	100 Parts	"	2650	1575		2.0
	Versamid 140	50 } 41.2 phr					
	N-Methyl Morpholine	10 }					
230	Same as #229, except	83.5 phr	"	773	1458		2.5
231	Same as #229, except	167 phr	"	373	894		2.0

* Not tested because of poor performance at -320°F

Table 18 (Continued)

Code	Adhesive System	Contact Pressure Cure at RT, days	Tensile Shear Strength, psi		Tee Peel Strenght, lbs/1"	
			R.T.	-320°F	R.T.*	-320°F
235	X-298 100 Parts	5-6	1686	3050		8.0
236	Curing Agent 7111 24.6 phr Same as #235, except 50 phr	"	1090	2605		7.0
237	Same as #235, except 101 phr	"	648	1370		4.0
238	X-298 100 Parts	"	1898	1930		4.0
239	Curing Agent U 10 phr X-298 100 Parts	"	2195	2548		4.5
	Versamid 140 50⎱ 24.6 phr N-Methyl Morpholine 10⎰					
240	Same as #239, except 50 phr	"	1382	3990		7.5
241	Same as #239, except 101 phr	"	388	1324		2.0
242	X-299 100 Parts	5-8	2470	1900		5.0
243	Curing Agent 7111 30.7 phr Same as #242, except 50 phr	"	1824	2138		4.0
244	Same as #242, except 101 phr	"	595	950		3.0
245	X-299 100 Parts	"	23.5	319		0.5
246	Curing Agent U 12.5 phr X-299 100 Parts	"	2455	1732		3.5
	Versamid 140 50⎱ 30.7 phr N-Methyl Morpholine 10⎰					
247	Same as #246, except 62.5 phr	"	1252	2370		5.0
248	Same as #246, except 125 phr	"	442	1098		1.5
249	X-300 100 Parts	4-7	2780	1745		2.5
250	Curing Agent 7111 41.2 phr Same as #249, except 83.5 phr	"	2178	1734		4.0
251	Same as #249, except 167 phr	"	544	912		1.0
252	X-300 100 Parts	"	2801	1254		3.0
253	Curing Agent U 16.7 phr X-300 100 Parts	"	3715	1842		2.5
	Versamid 140 50⎱ 41.2 phr N-Methyl Morpholine 10⎰					
254	Same as #253, except 83.5 phr	"	1484	1714		3.5
255	Same as #253, except 167 phr	"	410	734		1.0

(Continued on next page)

* Not tested because of poor performance at -320°F

TABLE 18 (Continued)

Code	Adhesive System		Contact Pressure Cure at RT, Days	Tensile Shear Strength, psi		Tee Peel Strength, lbs/1"	
				R.T.	-320°F	R.T.*	-320°F
256	X-301 Curing Agent 7111	100 Parts 100 phr	3-6	2325	1320		3.0
257	X-302 Curing Agent 7111	100 Parts 100 phr	3-6	2152	1318		2.0
258	X-303 Curing Agent 7111	100 Parts 100 phr	3-6	2660	1466		2.5
259	X-304 Curing Agent	100 Parts 100 phr	3-6	2275	1544		2.0

* Not tested because of poor performance at -320°F

TABLE 19

A STUDY OF EPOXY POLYAMIDE ADHESIVE SYSTEMS
AT VERY LOW TEMPERATURES

Code No.	Adhesive	Cure @ RT, days	Tensile Shear Strength, psi		Tee Peel Strength, lbs/1"	
			-320°F	R.T.	-320°F	R.T.
Commercial Epoxy-Polyamide Adhesive						
--	Resin 3147/7125	6	1778 (+125°F (+180°F	3887 1281) 498)	3.0	1.8
Acid & Anhydride Cures for Epoxy Resins						
276	MNA 85 phr Epon 828 DMP-30 1%	65 hrs @150°F	184	2410	---	---
277	HHPA 85 phr Epon 828 DMP-30 1%	65 hrs @150°F	1630	1010	---	---
278	DSA 135 phr Epon 828 DMP-30 1%	65 hrs @150°F	1895	2130	---	---
279	MNA 101 phr DEN 438 DMP-30 1%	65 hrs @150°F	1797	2017	---	---
282	Epon 812 100 pbw 67 Adipic Acid 14 pbw Versamid 125 33	7	2028	1537	---	---
283	Same as #282, except 67 pbw Versamid 125	7	807	1006	---	---
284	Same as #282, except 136 pbw Versamid 125	7	220	529	---	---
285	Epon 828 100 pbw Adipic Acid 44.4 DBVIII 5	17.5 hrs @300°F	4232	2667	---	---
286	Epon 828 100 pbw Azelaic Acid 57.0 DBVIII 5	17.5 hrs @300°F	3422	3322	---	---

TABLE 19 (Continued)

Code No.	Adhesive	Cure @ RT, days	Tensile Shear Strength, psi		Tee Peel Strength, lbs/1"	
			-320°F	R.T.	-320°F	R.T.
287	Epon 828 100 pbw Isosebacic Acid 62.0 DBVIII 5	17.5 hrs @ 300°F	2037	2205	---	---
288	Epon 828 100 pbw Suberic Acid 53.0 DBVIII 5	17.5 hrs @ 300°F	3780	2825	---	---
Low Viscosity Polyamides						
346	Genamid 2000/Epon 828,30/70	14	1044	1458	---	---
347	Genamid 250/Epon 828, 35/65	14	1025	2109	---	---

The results of this work are also shown in Table 19. The epoxy-acid/anhydride reaction could not be made to proceed at RT with catalysis (DMP-30 and DBVIII). Curing 65 hours at 150°F or 17 hours at 300°F did not yield promising liquid nitrogen temperature bond strengths. Partial modification of the epoxy with adipic acid at elevated temperature, followed by completion of the cure with a polyamide at room temperature, did not prove promising.

F. Low Viscosity Polyamides

Two very low viscosity polyamide resins were obtained and used with an epoxy resin for bond preparation. The low viscosity was expected to allow for higher filler loading rates, reduced bonding pressure, and possible faster reaction rates. The data are shown in Table 19. These resins gave poorer ambient and -320°F physical properties than polyamides previously studied. No further work was conducted with these materials.

G. Trifunctional Epoxy Resins

A trifunctional epoxy resin was obtained (Shell X-801) and used with an amine (Shell Z) and also a polyamide (Versamid 125) for lap shear specimen preparation by curing at room temperature at contact pressure. Because all RT cured adhesives to date have shown rather poor strength at +180°F, it was anticipated that the trifunctionality of this system would produce a tighter crosslink, with attendant improvement in elevated temperature properties.

Bonded specimens employing Resin 3135/7111 were also prepared for control purposes. The data are shown in Table 20. The trifunctional epoxy resin tended to produce a marginal improvement in 180°F tensile shear strength when compared with the control. The polyamide produced a better cure than the amine. The RT and -320°F tensile shear strength were quite comparable with the control.

XIII. STUDY OF UNIQUE ADHESIVE SYSTEMS CONSISTING OF ELASTOMER SUBSTRATES IN RESIN MATRICES FOR APPLICATION AT VERY LOW TEMPERATURE

A. Polymeric Substrates

Some new and unique concepts in adhesive bonding and their effect on strength at very low temperature were studied. One concept was the physical orientation, or placement of relative adhesive constituents in a glueline during a bonding operation. For example, if the adhesive systems consists of a nylon and an epoxy resin, then it would be possible to maintain each of these as separate and discrete resinous constituents. One orientation might be to employ the nylon as a thin membrane film or substrate and bond it, in turn, to each faying surface of the adherend with an epoxy resin. Conversely, each faying surface of the adherend might be coated with nylon by some suitable technique and subsequently adhered, one to the other, by means of an epoxy resin adhesive substrate. See Figure 21.

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TABLE 20

TRIFUNCTIONAL EPOXY RESIN ADHESIVE SYSTEMS

Code No.	System	Cure @ RT Days	Tensile Shear Strength, psi		
			-320°F	R.T.	+180°F
Control	Resin 3135/7111	8	1480	3262	404
#354	Epon X-801/Versamid 125, 50/50	14	1320	3320	616
#355	Same as #354, except 50/85	14	1400	3632	570
#356	Same as #354, except 50/120	14	1496	3380	399
#357	Epon X-801/Shell Z, 100/34	11	459	874	394
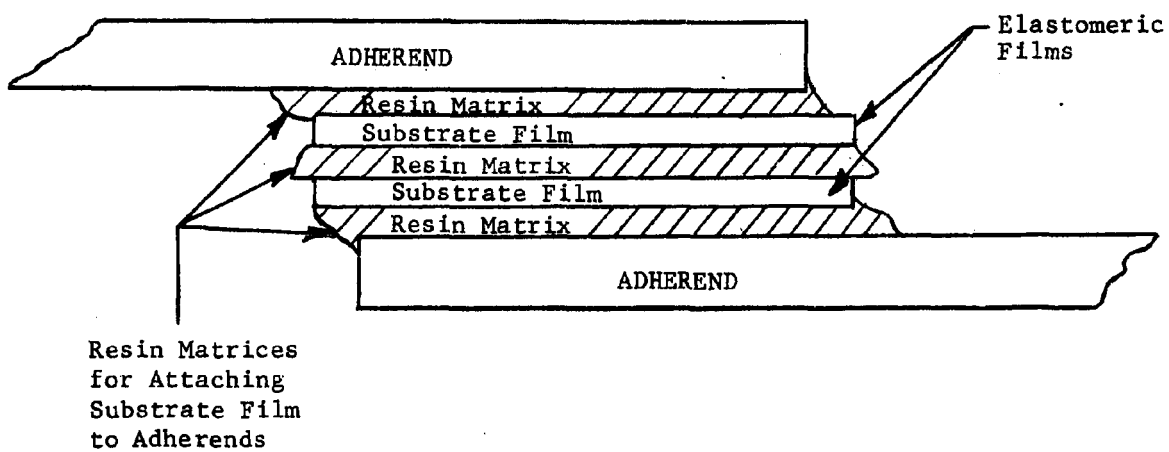
Figure 21. Cross Section of Composite Adhesive System

It has been pointed out that adhesives must demonstrate good strength (tensile shear) as well as toughness (tee peel). Usually, good strength pre-supposes one type of adhesive, and good toughness another; thus, in most adhesives two basic constituents are generally required (i.e., a rigid resin for strength, and an elastomer for toughness). Obviously, the relative place-ment of these multiconstituents, whether in homogeneous solution or heterogeneous form as resins and fillers, is very important to adhesive strength.

Various polymeric films selected as substrates were nylon, tetrafluoro-ethylene, fluoroethylene propylene, chlorotrifluoro ethylene, polyvinyl fluoride, silicone rubber, chlorobutyl rubber, hexafluoropropylene and vinylidine fluoride copolymer, vinylidene fluoride, urethane rubber, urethane esters, chlorosulfonated polyethylene, vinylidene chloride, and epoxy polyamide resin. Resin adhesives or matrices, for bonding the substrate to the adherends were Narmco Resin 3135 (epoxy polyamine), Metlbond 406 and 409 (nylon epoxy), unmodified nylon, and cyanoacrylate.

It was felt necessary to include the following selected variables in this study of composite adhesives so that as much helpful information as possible in developing a new adhesive might be gathered:

1. As many substrate materials as possible having good low-temperature properties so that selection of the best materials could be measured

2. Resinous adhesives for attaching the substrates to adherends which would develop optimum properties (nylon epoxy), even though the bonding techniques might be quite rigorous; also, types which required moderate bonding techniques (epoxy polyamide)

3. Effect of thickness of the substrate film on adhesive strength

4. Effect of multiple substrate layers on adhesive strength

5. Effect of crystallinity of substrate on adhesive strength

6. Effect of substrate surface treatment on adhesive strength

Table 21, Groups 1-16, shows the extremely interesting results obtained from this study. The particular compounding formulas are outlined. Curing was accom-plished at room temperature and contact pressure unless otherwise noted.

A promising adhesive system (Code #134, Table 21) consisting of two 1-mil substrate layers of Teflon FEP, Type A, with a sodium-naphthenate surface treat-ment and bonded to adherends with a room-temperature-curing epoxy polyamide adhesive (Narmco Resin 3135 and Curing Agent 7111) has been found to give a 20.0 lbs/1" tee peel strength at -320°F -- higher than any existing or experimental adhesive system known at this point. Since tee peel strength at low temperature is a coomon weak point of all existing adhesives, it is felt that this system is quite outstanding. The RT tee peel strength of this system is not too high, but might be adequate, particularly in view of the extremely good low-temperature properties. The tensile shear strength at RT and -320°F are good (2185 psi and 4012 psi, respectively).

TABLE 21

STUDY OF UNIQUE ADHESIVES SYSTEMS CONSISTING OF ELASTOMER SUBSTRATES
IN RESIN MATRICES FOR APPLICATION AT VERY LOW TEMPERATURE

Groups	Code	Elastomer Substrate Type	Surface Treatment	Resin Adhesive Type	Cure	Tensile Shear, psi* R.T.	-320°F	Tee Peel, lbs/1"** R.T.	-320°F
1	Beta_RT	Teflon TFE (tetrafluoroethylene), 4 mil.	Na-Naphthalene	Resin 3135 (epoxy-polyamide)	48 hrs at R.T.	2283	1765	10.0	5.0
	Beta_250	"	"	"	1 hr at 250°F	2763	3167	10.0	5.0
	#77	"	"	Metlbond 409(nylon epoxy)	1 hr at 350°F	2786	3035	20.0	3.5
	#86	"	Na-Amide	Narmco Resin 3135 (epoxy polyamide)	1 hr at 250°F	All bonds fell apart during handling			
	#79	Teflon FEP (fluoroethylene propylene) Type A	None	None	Heat fused at 600°F	706	3600 (4)	-	-
2	Gamma_RT	"	Na-Naphthalene	Resin 3135 (epoxy-polyamide)	48 hrs at R.T.	-	-	12.5	4.5
	Gamma_250	"	"	"	1 hr at 250°F	3008	5262 (4)	15.0	15.0
	#85	"	Na-Amide	"	"	753	447	0	0
	Zeta	"	Na-Naphthalene	Zytel 61 and resorcinol diglycidyl ether reaction product	1 hr at 350°F	598	3660	5.0	15.0

(Continued on next page)

TABLE 21 (Continued)

Groups	Code	Elastomer Substrate Type	Surface Treatment	Resin Adhesive Type	Cure	Tensile Shear, psi* R.T.	-320°F	Tee Peel, lbs/1"** R.T.	-320°F
2 (Cont.)	AEFF	Teflon FEP (fluoroethylene propylene) Type A	Na-Naphthalene	Caprolactone & propylene oxide cured with TP 440	1 hr at 250°F	1855	5583 (4)	10.0	6.0
	#133	Type A, 1-mil-one substrate layer	Na-Naphthalene	Resin 3135 (epoxy-polyamide)	5 Days at RT	2383	5405***	3.0	15.0
	#134	Same as #133, except two substrate layers (Adhesive B)	"	"	"	2185	4012	5.0	20.0
	#135	Type Exp.544,2 mil-one substrate layer	None	"	"	2538	4895	7.5	10.0
	#136	Same as #135 except two substrate layers (Adhesive B1)	"	"	"	2365	3912	7.5	10.0
	#178	Type 544,2-mil, 1 substrate layer	"	Eastman 910 (cyano-acrylate)	10 Days at RT	226	297	2.5	0
	#137	Same as #133, except 5 mil	Na-naphthalene	"	6 Days at RT	2310	5297***	4.0	10.0
	#138	Same as #134, except 5 mil	"	"	"	1790	2382	15.0	10.0
	#139	Same as #135, except 5 mil	None	"	"	2255	5342***	10.0	10.0
	#140	Same as #136, except 5 mil	"	"	"	1820	3022	15.0	5.0
	#141	Same as #133, except 10 mil	Na-naphthalene	"	"	1585	3352***	15.0	5.0
	#142	Same as #134, except 10 mil	"	"	"	1455	1911	2.5	10.0

(Continued on next page)

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TABLE 21 (Continued)

Groups	Code	Elastomer Substrate Type	Surface Treatment	Resin Adhesive Type	Cure at RT, Days	Tensile Shear, psi* R.T.	Tensile Shear, psi* -320°F	Tee Peel, lbs/1"** R.T.	Tee Peel, lbs/1"** -320°F
2 (Cont.)	#210	Two films Teflon FEP, Type 544, 1 mil	None	Resin 3174/7125	7	1808	1024	1.0	3.0
	--	"	None	Resin 3135/7111	5	2185	4012	5.0	20.0
	--	"	Na-Naphthalene	"	3	--	--	--	7.5
	#274	Same as #210	Aluminum metallized	"	4	1321	1258	--	3.2
	#268	Same as #210	None	Adiprene L100, 11 phr Moca	10	1496	3755	17.2	6.5
	#269	Same as #268	None	Adiprene L167, 20 phr Moca	10	1680	3775	25.0	3.5
	#270	Same as #268	None	Adiprene L213, 25 phr Moca	10	2182	2317	5.5	6.5
	--	Adhesive B	--	--	5	4015	2277	--	--
	--	Adhesive B, except films stretched 50% orig. length	--	--	5	2475	1970	--	--
	--	Adhesive B	Films cleaned with sodium dichromate & H_2SO_4 until they held water film	--	2	2287	1652	4.5	--
	#303	1-mil Teflon FEP, Type 544 fused to each adherend surface	None	Resin 3135/7111	2	1117	902	1.5	0.4
	#305	Two films Teflon FEP, 1-mil	Commercial Etch	Resin 3135/7111	11-18	2025	4925	4.1	9.0
	#308	Two films Teflon FEP, 1 mil	Bondaid Etch	"	11-18	1607	3192	2.7	6.0

TABLE 21 (Continued)

Groups	Code	Elastomer Substrate Type	Surface Treatment	Resin Adhesive Type	Cure	Tensile Shear, psi* R.T.	Tensile Shear, psi* -320°F	Tee Peel, lbs/1"** R.T.	Tee Peel, lbs/1"** -320°F
	#82	Kel-F(chlorotrifluoroethylene) 4 mil	Na-Naphthalene	Resin 3135 (epoxy-polyamide)	1 hr at 250°F	2575	5002***	10.0	17.5
	#83	"	"	Metlbond 406 (nylon epoxy)	1 hr at 350°F	2230	4848***	7.5	17.5
	#87	"	Na-Amide	Resin 3135 (epoxy-polyamide)	1 hr at 250°F	353	225	Bonds fell apart	
	#126	4.5 mils-one substrate layer	Na-Naphthalene	Resin 3135 (epoxy-polyamide)	8 Days at RT	2182	3172	7.5	7.5
	#127	Same as #126, except two substrate layers	"	"	"	1831	3030	2.5	2.5
3	#128	Same as #126, except quenched from melting point to make small crystalline structure (amorphous)	Na-Naphthalene	Resin 3135 (epoxy-polyamide)	8 Days at RT	2738	3615	4.0	2.5
	#129	Same as #126, except cooled very slowly (50°F per hr) from melting point to make large crystalline structure (crystalline)	"	"	"	2622	2956	5.0	5.0
	#130B	Same as #126, except 8.5 mils	"	"	"	3004	4570	5.0	5.0
	#131B	Same as #127, except 8.5 mils	"	"	"	3215	1856	5.0	6.5
	#289	One film Kel-F82, 4 mil	Na-Naphthenate	Resin 3135/7111	5 Days at RT	4445	2712	8.0	4.2

TABLE 21 (Continued)

Groups	Code	Elastomer Substrate Type	Surface Treatment	Resin Adhesive Type	Cure	Tensile Shear, psi* R.T.	-320°F	Tee Peel, lbs/1"** R.T.	-320°F
3 (Cont.)	#290	Same as #289, except Kel-F 8110, 9-1/2 mil	Na-Naphthenate	Resin 3135/7111	5 Days at RT	3305	2972	8.0	2.1
	#291	Same as #289, except Kel-F 8205, 5 mil	"	"	"	3120	2600	9.0	6.2
	#306	Two films Kel-F, 1 mil	Commercial Etch	"	11-18	1597	3837	1.6	4.5
4	#160	Tedlar (polyvinyl fluoride), Type A40, 2-mil, one substrate layer	None	Resin 3135 (epoxy polyamide)	16 Days at RT	2297	1573	5.0	2.5
	#161	Same as #160, except Type A20	"	"	2 Days at RT	1735	1050	0.5	Failed in handling
	#162	Same as #160, except Type AP-20WH	"	"	"	1181	954	Failed in handling	
	#163	Same as #160, except 4-mil and Type AP40WH	"	"	"	2847	1173	4.0	1.5
	#164	Same as #160, except 4-mil	"	"	"	2022	1504	3.5	2.0
	#165	Same as #160, except Type AP-20WH	"	"	"	381	287	Failed in handling	
	#166	Same as #160, except 4-mil and Type AP40WH	"	"	"	2547	1400	2.5	2.0
5	-	Saran 723 (Vinylidene chloride)	Na-naphthalene (Treatment disintegrated film)	-		-	-	-	-

(Continued on next page)

TABLE 21 (Continued)

| Groups | Elastomer Substrate | | | Resin Adhesive Type | Cure | Tensile Shear, psi* | | Tee Peel, lbs/1"** | |
	Code	Type	Surface Treatment			R.T.	-320°F	R.T.	-320°F
	#73	Nylon FM 63 (nylon)	None	Resin 3135 (epoxy-polyamide)	48 hrs at RT	1043	698	0	0
	#80	Zytel 61(nylon copolymer)	"	"	"	1507	701	0	0
6	#81	"	Tolylene di-isocyanate	"	"	1210	811	1.0	0
	#74	Narmco Resin 3135 (epoxy polyamide)	None	Zytel 61 nylon film fused to adherends at 400°F	"	1228	806	0	0.5
7	#75	CSC #3801 (RTV silicone rubber)	"	Metlbond 409 (nylon epoxy)	1 hr at 250°F	126	2260	0.5	2.0
8	#89	MD-551(chloro-butyl rubber)	"	Resin 3135 (epoxy polyamide)	1 hr at 250°F	314	2252	5.0	5.0
9	#90	Viton A-HV(Hexa-fluoropropylene and vinylidene fluoride co-polymer	"	"	"	1371	***4820	19.0	7.5
10	#84	Kynar (vinyl-idene fluoride)	Na-Naphtha-lene	Metlbond 406 (nylon epoxy)	1 hr at 350°F	1740	1327	15.0	2.5
11	#88	Adiprene C (urethane rubber)	None	Resin 3125 (epoxy-polyamide)	1 hr at 250°F	2598	3785	15.0	10.0
	#152	50% Adiprene C as in #88, 50% Vitron A as in #90(cured 30 min at 300°F)	"	Resin 3135 (epoxy polyamide)	7 Days at RT	59	725	1.5	0

(Continued on next page)

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TABLE 21 (Continued)

Groups	Code	Elastomer Substrate Type	Surface Treatment	Resin Adhesive Type	Cure	Tensile Shear, psi* R.T.	-320°F	Tee Peel, lbs/1"** R.T.	-320°F
11 (cont.)	#153	50% Adiprene C as in #88, 50% Kel-F 800 (cast from tetrahydrofuran, cured 30 min at 300°F)	None	Resin 3135 (epoxy-polyamide)	7 Days at RT	576	1484	20.0	1.5
	#353	One film UR80T urethane elastomer 9 mil	"	Resin 3135/7111	4 Days at RT	1031	1132	16.6	1.5
12	#93	Thiokol FA (polysulfide rubber)	"	"	1 hr at 250°F	128	1292	7.5	2.5
13	#91	Syntex 3398 (urethane ester)	"	"	"	306	752	2.5	1.0
14	#92	Hypalon (Chlorosulfonated polyethylene)	"	"	"	2838	***4392	15.0	4.0
15	#179	Mylar Type A (polyester) 2-mil single substrate layer	"	Resin 3135 (epoxy-polyamide)	5 Days at RT	749	795	0	2.5
16	#187	Aclar Type 22A (fluorohalocarbon) 2 mil, single substrate layer	Na-naphthalene	Resin 3135 (epoxy-polyamide)	4-8 Days at RT	1568	1469	5.0	9.5
	#188	Same as #187, except Type 22C	"	"	"	1948	2315	7.5	3.0
17	#94	Copper foil (2-mil)	Dilute nitric acid	"	7 Days at RT	1376	994	2.5	5.0
	#97	"	15 cc 40% FeCl3, 30cc 15 N HNO3 197 cc H2O	Metlbond 406 (nylon epoxy)	15 Min @350°F	4062	2148	10.0	7.5

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TABLE 21 (Continued)

Groups	Code	Elastomer Substrate Type	Surface Treatment	Resin Adhesive Type	Cure	Tensile Shear, psi* R.T.	Tensile Shear, psi* -320°F	Tee Peel, lbs/1"** R.T.	Tee Peel, lbs/1"** -320°F
18	#95	Lead foil (4-mil)	Dilute nitric acid	Resin 3135 (epoxy-polyamide)	7 Days at RT	1696	705	5.0	0.5
	#98	"	15 cc 40% FeCl3, 30cc 15 N HNO3 197 cc H2O	Metlbond 406 (nylon epoxy)	15 Min at350°F	900	598	5.0	1.0
	#99	Same as #98, except film annealed below melting point	"	"	"	1288	597	2.5	1.0
	#105	Lead foil (4-mil)	Copper stripe, silver plate	Resin 3135 (epoxy-polyamide)	2 Days at RT	1121	467	0	3.0
	#106	"	"	Metlbond 406 (nylon epoxy)	15 Min at350°F	682	510	7.5	2.0
	#260	One substrate lead foil,4 mil	None	Resin 3135/ 7111	10-11 Days at RT	501	1238	5.0	1.5
19	#103	Tin foil (4-mil)	None	Resin 3135 (epoxy polyamide)	2 Days at RT	2355	2206	4.5	3.0
	#261	One substrate tin foil, 4 mil	None	Resin 3135 7111	10-11 Days@RT	602	3812	3.0	4.5
20	#104	Cadmium foil (4-mil)	"	"	"	1518	870	1.0	1.0

(Continued on next page)

TABLE 21 (Continued)

*   Average of four (4) specimens

**   Single specimens

***   Failure in metal adherends (i.e., "pull-out" of 3/8)

All bonding pressures were 25 psi.

Elastomer Substrate Formulation and Cure

#88	Adiprene C	100	#89	Chlorobutyl MD-551	100
	MBTS	4		MgO	2
	MBT	1		Benzothiazyl Disulfide	2
	Activator RCD 2098	.35		Tetramethyl Thiuram Disulfide	1
	Sulfur	.75		ZnO	3
#90	Viton A.HV	100	#91	Syntex 3398	619
	MgO	15		Manganese Naphthenate 6%	.6
	Diak No. 1	1		Activ-8	.2
#92	Hypalon 40	100	#93	Thiokol FA	100
	Epon 828	15		MBTS	.3
	MBTS	.5		ZnO	10
	Tetrone A	1.5			

Above substrate formulations all cured 30 minutes at 310°F.

Other substrate materials, including Kel-F, Adiprene C, etc., demonstrated very good potential in composite adhesives for application at extremely low temperature. The success that elastomeric substrates have contributed to toughness of these adhesives at low temperature can probably be attributed to the comparatively good elongation of such materials.

It was extremely encouraging to note that the room-temperature-curing epoxy polyamine resin yielded almost equivalent data to the nylon-epoxy when used for bonding substrates to adherends in composite adhesives. When the composite adhesive is stressed in tension (tensile shear), the whole cross section functions as a homogenous material and the failure occurs at the weakest point -- the surface treatment on the fluorocarbon plastic film, for example. When the composite adhesive is stressed in peel (tee peel), the components of the composite function independently and the elastomeric substrate tends to redistribute stresses, with failure occurring at the same point as in tension. This is fortunate, for it allows use of the epoxy polyamine system with attendant simplified processing and without significant sacrifice to physical properties.

The effect of thickness of substrate films was studied in the cases of Teflon FEP and Kel-F. Although not completely conclusive, an increase in film thickness from 1 to 10 mils tended to reduce tee peel strength at -320°F from 15.0 to 5.0 lbs/1". The tensile shear strength at RT and at -320°F tended to be lowered by an increase in film thickness. The effect of multiple substrate layers was even less conclusive; however, multiple layers tended to reduce tensile shear strength and, at the same time, increase the peel strength.

Kel-F film was obtained in approximate thickness of 4 mils in order to study crystallinity. Two pieces of this film were heated in an oven at 500°F for one-half hour -- slightly above the softening point. One piece was withdrawn and quickly cooled by quenching in water. This procedure is said to produce very small crystals and yield the most amorphous material attainable (9). The appearance of the resultant film revealed a distinct degree of clarity, indicating that rapid cooling had prevented excessive crystal growth. The other piece of film was cooled slowly in the oven (50°F/hour) to allow the growth of comparatively large crystals. The appearance of the resultant film was opaque. Each film was given a sodium-naphthalene surface treatment for bonding. This was followed by bonding the substrate film in a glueline using Resin 3135 epoxy polyamine adhesive and curing at room temperature. Testing of these specimens yielded quite the reverse from anticipated results. The non-crystalline or amorphous material gave lower -320°F tee peel strength and higher -320°F tensile shear strength than the crystalline material. The margin of difference, however, was quite small.

A study of surface treatment for fluorocarbon plastic substrates included sodium-naphthalene (10), sodium-amide (11) and a cementable surface applied by the manufacturer to the Teflon FEP, Type Exp. 544. The sodium-amide was applied in the laboratory but failed to leave a deposit on the films. The resultant treatment was ineffective for bonding. It was found that the cementable surface, Type Exp. 544, was equivalent in every way to the sodium-naphthalene surface. Since it is commercially available, it should be recommended.

Some additional data have been reported for polymeric composite adhesive systems at cryogenic temperature by Lockheed-Georgia Company, Marietta, Georgia (12).

B. Selection of Adhesive B

The adhesive consisting of two 1-mil substrate films of Teflon FEP, Type 544, bonded at RT and contact pressure in an epoxy-polyamide resin matrix with Narmco Resin 3135 and Curing Agent 711(referred to in Table 21, Code #134) was selected for further evaluation and study because it demonstrated the best all-around balance of strength-to-toughness properties over the temperature range from ambient to -423°F of any room-temperature curing adhesive evaluated. This system was designated as Adhesive B.

C. Improvement Studies for Composite Polymeric Adhesives

Resin 3147/7125 was used to replace the Resin 3135/7111 epoxy polyamide in Adhesive B, and subsequently utilized two 1-mil substrate films of Teflon FEP, Type 544. Tensile shear and tee peel strengths were appreciably lower than in Adhesive B, both at ambient and low temperature. No advantage could be seen for the resin replacement. See Table 21 (Code #210).

Further work with Adhesive B (the composite system consisting of two substrate films of 1-mil Teflon FEP, Type 544, in an epoxy-polyamide resin matrix) revealed considerable data scatter in tee peel strength. The bonds tended to fail in adhesion to the cementable Teflon surface, and it was difficult to maintain the 20.0 lbs/1" tee peel strength originally quoted. Therefore, it was suspected that the cementable surface of the Teflon varies from batch to batch of film. Tensile shear strength did not appear to be noticeably affected.

It was originally reported that a sodium naphthalene surface of Teflon FEP was every bit equivalent to the Type 544 surface. This was found to be inaccurate when the quality of the Type 544 surface varies. An experiment was performed to check the quality of a questionable lot of 1-mil Teflon FEP, Type 544. Tensile shear and tee peel specimens were prepared with Adhesive B, utilizing the lot of questionable film as control. The same film was given a sodium naphthalene etch and specimens were prepared from them, utilizing Adhesive B techniques. The data are compared in Table 21.

It was concluded that the batch of Type 544 Teflon FEP film under question was indeed faulty. It could not be adhered-to sufficiently by itself, and a sodium naphthalene etch did not improve adhesion.

Since the cementable surface of the Teflon FEP, Type 544, was suspected to vary in quality, it was thought that other surfaces might cause better adhesion. Chemically pure aluminum was vacuum-deposited in our laboratories on both sides of Teflon FEP, Type 544, film. It was anticipated that the adhesion of aluminum to the Teflon might be better than the adhesion of the epoxy-polyamide resin now being employed. Tensile shear and tee peel specimens were prepared in a manner similar to Adhesive B and tested at ambient and liquid nitrogen temperatures. These data are also reported in Table 4, Code #274. Metallizing the surface of Type 544 Teflon did not improve the bondability. Further work in this particular area was not conducted.

Since Adhesive B has performed exceedingly well at extremely low temperature, it was thought that further improvement in the composite adhesive might be effected by replacing the epoxy-polyamide resin with a polyurethane resin for adhering the fluorocarbon substrate films. Test specimens(Code #268, 269, and 270)were prepared. Similarly, it was thought that a polyurethane resin might be better for adhering metallic substrate films than the epoxy-polyamide system. The metallic substrates were chemically pure lead and tin. Test specimens(Code #260 and 261)were accordingly prepared. Tensile shear and tee peel tests were made at -320°F and RT. The data are shown in Table 21.

Replacing the epoxy-polyamide resin with a polyurethane elastomer in Adhesive B and where metallic substrates were used did not improve the strength of composite adhesives.

Films of Kel-F 81 and 82 were obtained in thicknesses ranging from 4 to 10 mils. These were given the standard sodium-naphthalene etch and subsequently used as single substrates in an epoxy-polyamide matrix (Resin 3135 and Curing Agent 7111) for bonding 7075-T6 bare aluminum. The resultant data are also shown in Table 21. The bond strengths, particularly the peel strengths, were not as good at extremely low temperature as those with Teflon FEP.

In another experiment, 1-mil Teflon FEP, Type 544, was heat-fused to the adherend surfaces of tensile shear and tee peel specimens. The coated metal was then subsequently bonded at room temperature and contact pressure with Resin 3135 and Curing Agent 7111. The adhesive strength and toughness were far inferior, both at ambient and very low temperature, than when the Teflon was employed as a substrate film, as, for example,Adhesive B. The results are shown in Table 21.

Discussions were held with DuPont people regarding the bondable surface of Teflon FEP, Type 544, resulting in the following comments:

a. The Type 544 cementable surface is applied to the film in a 2-step process. The side treated first is layed against the separator and wound towards the core of the roll. The side treated last is on the outer side of the roll.

b. The Type 544 surface may be quite perishable (i.e., the side treated first may be less easily adhered-to than the side treated last).

c. Users are cautioned to avoid contamination of the cementable surfaces, particularly where one side is bonded before the other.

d. Stretching of the film is reported to result in poorer adhesion than if the film is not stretched prior to, or during, the bonding operation.

Past experience has shown that Teflon TFE with a sodium amide or sodium naphthalene etched surface will hold a water film. This is a necessary requirement for most adhesive bonding, particularly for metal surfaces. However, this was not found to be true with the Type 544 cementable surface of Teflon FEP. An experiment was conducted to make the Type 544 surface hold a water film. The film was cleaned with a sodium dichromate sulfuric acid solution identical to that used for cleaning 7075-T6 aluminum alloy adherends. The film subsequently held a water film;

however, when bonds were made with it in a manner used for Adhesive B, the bond strengths were considerably poorer than prior to such treatment. Results are shown in Table 21.

Another experiment was conducted to determine the effect of stretching 1-mil Teflon FEP, Type 544, on adhesive strength. The film was stretched 50% (half again its original length), then two such films laminated in an epoxy-polyamide matrix between 7075-T6 bare aluminum adherends using a RT cure at contact pressure. The results are also shown in Table 21 under "Composite Adhesive Systems." It was concluded that stretching significantly reduced the ability to adhere to Teflon FEP, Type 544. While stretching resulted in reduced film thickness, past experience indicates this could not be responsible for the reduced adhesive strength noted.

No solution has been found to assure the reliability of adhesion to cementable Teflon film.

Commercially-etched grades of 1-mil Teflon FEP and 1-mil Kel-F films were obtained for the purpose of comparison with existing data when employed in composite adhesives. A commercial etchant for halocarbons (Bondaid) was also obtained and applied to 1-mil Teflon FEP, Type A. The resulting film was employed in a composite adhesive and the data compared with existing data.

Table 21 shows the results of this work. The commercially-etched films of Teflon FEP and Kel-F showed poorer adhesive properties (particularly peel strength at very low temperature) than data already presented for other films. The commercial etchant for Teflon FEP did not produce as good results as the Type 544 commercial treatment.

A room temperature curing polyester resin was used to replace the epoxy polyamide resin in the composite system Adhesive B for laminating the Teflon films in the glueline. Table 21 shows that the polyester produced far inferior adhesive results than the epoxy polyamide resin.

A commercial grade of polyurethane film, probably based upon Texin,* was obtained and used for composite adhesive bonding with Resin 3135/7111. The data are shown in Table 21. No advantage could be seen in using polyurethane substrates in bonding.

D. Metallic Substrates

Because of the very excellent adhesive properties demonstrated by the foregoing substrate films at extremely low temperature, it was quite natural to seek other materials with better elongation in hopes that the tee peel might be upgraded. The chloro-fluorocarbons and fluorocarbons at very best have an elongation of 0 (13) to 0.5 (14) in a 2"-gage-length at $-320°F$. By direct comparison, some metals have very attractive low temperature properties. It was thought that some of these might perform extremely well as elastomer substrates in resin matrices for adhesive systems designed for very low temperature. Pure lead,

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*Mobay Chemical Co.

for example, has an elongation of about 36% (13) at -320°F. In fact, the elongation of lead increases on lowering the temperature from -320°F to -423°F. Other promising metals include tin and copper. It was felt that the advantages in elongation which these materials had over polymers could be made to enhance the tee peel characteristics of adhesives at very low temperature.

In this second study of substrate films, the following metals were selected: copper, lead, tin, and cadmium. All were commercially pure. The copper was obtained as a 2-mil film; the other films were produced by rolling on a conventional laboratory mill. It was expected that some of these metals would be difficult to bond to, so several surface treatments were evaluated. Copper was given a nitric acid etch, and a nitric acid and ferric chloride treatment. Lead was given the same treatment and, in addition, a bright silver-plate. Tin and cadmium were used without treatment. Lead was evaluated in the annealed as well as unannealed condition to gain the maximum low temperature elongation.

Two resin matrix systems were employed -- Metlbond 406 nylon-epoxy with a 350°F cure, and Resin 3135 epoxy polyamine with a room temperature cure. It was felt that the former system would allow stressing the metal substrate film to its ultimate strength, whereas the latter system most closely approximates the non-production-line type of adhesive sought by NASA in this work.

The second portion of Table 21, Groups 17-20, gives the results of this study. None of the composite adhesives employing metallic films as elastomer substrates performed as well as the fluorocarbon substrates. This was true for tensile shear as well as tee peel, both at RT and -320°F. The failure of these systems is believed to be largely the inability to adhere sufficiently to the substrate with polymeric adhesives to stress the metal to its ultimate strength. The bond failures, which bear this out, were predominantly adhesion failures to the substrate (i.e., adhesion to either the bare metal or the surface treatment applied to the metal).

E. Metallic Solder Bonds

To prove the utility of metallic substrate films such as lead and tin for adhesive bonding at extremely low temperature, it was deemed necessary to determine the tensile shear and tee peel strength properties of these pure metals when employed as solders. Soft annealed copper was selected as the adherend material -- .064" thickness for 1/2" overlap tensile shear specimens, and .020" thickness for tee peel specimens. The bonding surfaces were mechanically cleaned, "tinned" with the aid of flux with chemically pure lead and tin; and surfaces subsequently mated and fused together. Table 22 (Code #264 and 265) shows the results of this work. The lead solder bonds were very poor because of oxidation during the bonding operation. The tin shear and peel strengths were quite good at low and ambient temperature, but not as good as strengths reported for polymeric adhesives. At this point, there was not sufficient promise for metals as adhesive constituents for extremely low temperature to justify more work along these lines. It was postulated that the modulus of metals is too high to be considered worthy of combination with high polymers.

TABLE 22

METALLIC SOLDER BONDS

Code	System	Tensile Shear, psi		Tee Peel, lbs/1"	
		-320°F	R.T.	-320°F	R.T.
264	Metallic Lead Solder, Copper Adherends	2810	1208	Premature failure (oxidized solder)	
265	Metallic Tin Solder, Copper Adherends	2882	3228	13.0	30.0

XIV. A STUDY OF MISCELLANEOUS ADHESIVES, ELASTOMERS AND RESINS FOR ADHESIVE BONDING AT VERY LOW TEMPERATURE

A. Commercial Adhesives

Tensile shear and tee peel strengths were determined at RT and -320°F for a manufacturer's batch revision of FM-1000 nylon-epoxy adhesive. This material was evaluated with and without the recommended primer, and strength was compared with a previous batch of the same adhesive. Cure was accomplished at 350°F. A 25% increase in -320°F tee peel strength was noted for the revised adhesive without primer.

Eastman 910 cyanoacrylate adhesive was also evaluated. This system proved extremely troublesome when used with the catalyst necessary for RT cure because of the extremely fast polymerization rate. Table 23 shows the results of this work. The strengths were not promising.

B. Polysulfide Modified Epoxies

A liquid polysulfide rubber was used to modify an epoxy resin at a 50 and also a 200 phr level, followed by curing at RT with an amine. Tensile shear and tee peel specimens were prepared with the modifications and tested at RT and at the liquid nitrogen point. Table 23 shows the results of this work. Polysulfide modification of the epoxy resin resulted in lowering of tensile shear strength at RT and -320°F. Tee peel strength was significantly improved at the higher polysulfide level at RT, but only mediocre improvement was noted at cryogenic temperature. No improvement in adhesive cryogenic properties could be gained with polysulfide modification.

C. RTV Silicone Elastomers

A series of commercial, room-temperature-vulcanizing, silicone rubber adhesives were obtained, used for bond preparations, and the resulting specimens evaluated at RT and the liquid nitrogen temperature. The results of this study are shown in Table 23. In general, the tensile shear and tee peel strengths for these systems were below acceptance at RT and only mediocre at -320°F when compared with other adhesives previously studied.

D. Miscellaneous

PRDA, a phenoxy-8 thermoplastic, and Mylar polyester were used for the modification of epoxy, epoxy-polyamide, and nylon-based adhesive systems. The modifiers were incorporated by solution techniques using dimethylformamide, or by milling. Curing temperatures were necessarily high (up to 350°F) to induce fusion and bonding. The results are shown in Table 23. Results were not promising.

E. Halogenated Nylons

Knowing the outstanding low temperature improvements that can be effected by fluorinating polyethylene, it was decided to investigate the properties of halogenated nylons.

TABLE 23

A STUDY OF MISCELLANEOUS ADHESIVES, ELASTOMERS AND RESINS
FOR ADHESIVE BONDING AT VERY LOW TEMPERATURE

Code	Adhesive System (weight ratios)	Cure	Tensile Shear, psi*		Tee Peel, lbs/1"**	
			R.T.	-320°F	R.T.	-320°F
-	**Nylon-Epoxy** FM-1000, Batch 250, No Prime	1 Hr at 350°F	6542	4498	32.0	7.2
-	FM-1000, #62-3386 and 62-3387. Primed	1 Hr at 350°F	7226	2666	85.0	9.0
-	FM-1000, #62-3389, and 62-3390, No Prime	1 Hr at 350°F	7190	4275	67.5	10.0
177	**Cyanoacrylate** Eastman 910 plus Eastman catalyst	10 Days at RT	172	175	Failed during Handling	
326	**Polysulfide Modified Epoxies** Epon 828/Thiokol LP-3/DMP-30 100/50/10	6 Days at RT	817	560	Failed in Handling	
327	Same as #320, except 100/200/10	6 Days at RT	925	1394	17.0	2.0
320	**Silicones** DC Q-2-0103-2 plus DC A-4014 prime	6 Days at RT	157	3315	8.5	4.5
321	DC RTV 11 plus 25P6/A-1100 prime	6 Days at RT	163	3168	2.0	3.5
322	GE RTV-40 plus GE XS-4004 prime	6 Days at RT	38	240	1.25	1.0
323	GE RTV-60 plus XS-4004 prime	10 Days at RT	339	4110	---	---
348	Silastic DC 140, DC 1200 Primer	7 Days at RT	2682	330	7.9	9.25

(Continued on next page)

*   Average of 4 specimens
** Single specimens

TABLE 23 (Continued)

Code	Adhesive System (weight ratios)	Cure	Tensile Shear, psi*		Tee Peel, lbs/1"**	
			R.T.	-320°F	R.T.	-320°F
	Silicones (continued)					
349	Silastic DC Q-0-0002A/B DC 1200 Primer	7 Days at RT	3765	470	7.0	7.3
350	Silastic DC Q-0-0002A/B DC 1200 Primer	7 Days at RT	1907	310	1.0	3.6
	Miscellaneous					
Q	PRDA/Epon 828/dicyandiamide, 100/33/3	1 Hr at 350°F	4510	3795	5.0	4.0
R	PRDA/Epon 828/dicyandiamide, 100/50/3	1 Hr at 350°F	5220	3620	-	-
MY1	Mylar/Resin 3135, 25/100, cast from DMF solution	1 Hr at 300°F	2268	1754	12.5	3.5
MY2	Mylar/Resin 3135, 50/100, cast from DMF solution	1 Hr at 300°F	2335	705	-	-
M1	PRDA/Zytel 61, 100/25, cast from DMF solution	1 Hr at 300°F	2588	2318	-	-
N	PRDA/Zytel 61, 100/25, milled	1 Hr at 350°F	3632	1861	10.0	2.5
O	PRDA/Mylar, 100/25, milled	1 Hr at 350°F	3207	3522	10.0	5.0

* Average of 4 specimens
** Single specimens

TABLE 23 (Continued)

| Code | Adhesive System (weight ratios) | Halogenated Nylons | | Cure | Tensile Shear psi* | | Tee Peel, lbs/1"** | |
		Nylon Softening Point, °C	Percent Halogen in Nylon		R.T.	-320°F	R.T.	-320°F
157	Hexafluoroglutaryl chloride 0.2 mole, hexamethylene diamine 0.2 mole.... 75 pts Epon 828 prereacted with dicyandiamide ....25 pts	184	-	1 Hr at 400°F	1146	814	-	-
158	Chlorinated Zytel 61.......... 75 pts Epon 828 prereacted with dicyandiamide .... 25 pts	-	37.0	1 Hr at 350°F	2435	998	1.0	0.5
159	Brominated Zytel 61.......... 75 pts Epon 828 prereacted with dicyandiamide .... 25 pts	-	33.6	1 Hr at 350°F	462	468	Failed in Handling	

* Average of 4 specimens

** Single specimens

A fluorinated nylon was prepared by reacting 0.2 mole of hexafluoroglutaryl chloride with 0.2 mole of 1,6 hexane diamine by the previously reported techniques of interfacial polymerization. After purification, the softening point of the nylon was determined to be 184°C. An adhesive was prepared from the polymer by mixing 3 parts with 1 part of a prereacted epoxy resin (Epon 828 with 6 phr dicyandiamide prereacted to a gel time of about 3 minutes at 350°F). Test specimens were prepared from the adhesive by bonding at 400°F.

Zytel 61 nylon copolymer was chlorinated in the presence of ultraviolet light by bubbling chlorine through a water suspension of the finely divided nylon. After purification, the chlorine content was determined to be 37.0%. An adhesive was prepared in the same manner described above.

Zytel 61 nylon copolymer was also brominated in the presence of ultraviolet light using bromine water. After purification, the bromine content was determined to be 33.6%. An adhesive was prepared in the same manner described above.

The results of initial halogenation studies (see Table 23) of several nylons have failed to show any improvement in low temperature properties as compared with their non-halogenated counterparts. Work has been too meager to evaluate the potential of this approach.

XV. STUDY OF POLYURETHANE AND MODIFIED SYSTEMS AS ADHESIVES FOR VERY LOW TEMPERATURE APPLICATION

A. Polyurethane Prepolymers

A series of polycaprolactones have been prepared by the homopolymerization of caprolactone. It has been reported that these polymers have unusual low-temperature properties in urethane formulations. Samples with molecular weights of 1800 and 3400, and samples of approximately 10,000 and 20,000 were prepared by means of tetrabutyltitanate catalysis. Triethyleneglycol was used as a starter. Prepolymers were then prepared by reaction of the hydroxyl terminated polycaprolactones with methylene bis (4 phenylisocyanate). Excess isocyanate is used so that the final prepolymer has 14 percent by weight unreacted NCO content. Various reactants can then be used to cure the system.

Initial attempts to evaluate the influence of the molecular weight of the polycaprolactone upon the performance of the final adhesive indicated that little difference is noted in adhesive strength at room temperature and at -320°F. This is shown in data from systems AD, AH, AK, and AM. These were prepared by accomplishing final cure of the prepolymer with polyol TP-440. AD was formulated with polycaprolactone with the lowest molecular weight of 1800, and AM used the polycaprolactone with the highest molecular weight of 10,000. All four have excellent low-temperature strength and it is indicated that the polycaprolactone with a molecular weight of 1800 produces the best results. It might be pointed out that an autoclave was required to cure these systems in order to avoid blowing. While this is impractical for field application, it was used to arrive at the maximum strength possible from these systems. AA and AE are two of the same systems cured at 250°F at atmospheric pressure.

Other curing agents were used including "Moca," triethylene glycol, and trimethylol propane. See Table 24. Adhesive strength was poor and, in the case of "moca", gelation was much too fast to prepare good bonds.

A similar prepolymer with 10 percent free NCO was prepared with polyol TP 740 and MDI. Bonds were then prepared by final curing with additional TP 440 and TP 740. Excellent results were obtained and data are shown in Table 24 under AY and BD. Note that the lower molecular weight polyol (TP 440) gives expected higher room temperature shear and curing, while TP 740 gives higher room temperature peel. Surprisingly, both have the same -320°F peel strength.

An unusual polyester-polyether was prepared with proplyene oxide and caprolatone using triethylene glycol as a starter and BF_3 catalysis. The polymer has the structure indicated below:

HOXXX-YXXYXYXXYYRYYYXYYXYXXY--XXXOH

This chain has varying composition, progressing from the R group to the ends. It was hoped that this design would lower the crystallization tendency and result in improved low-temperature flexibility. Results shown in Table 24 (AP, AQ) were not encouraging with this attempt.

A small amount of tetramethylbutanediamine was used to catalyze the TP 740-MDI system (AZ) with a room temperature cure. Surprisingly good results were obtained and further study of room temperature curing polyurethanes is warranted. A similar resin (BE) gave a poor showing.

B. Non-Prepolymer Polyurethanes

Data in Table 25 are systems obtained by a one-step reaction of the isocyanate with the polyol. In order to obtain an idea of the ultimate strength of these systems, all bonds were prepared in an autoclave.

A comparison of AV and AW indicates that MDI gives a slightly better performance in room temperature shear and peel. A comparison of AW with BD in Table 24 indicates that the prepolymer method gives slightly better results, probably due to more controlled linear chain extension which generally improves tensile strength. AU and AV demonstrate again the fact that the more flexible, higher molecular weight TP 740 gives better low-temperature performance. Polyol LHT 240 was formulated in AX with results similar to TP 740.

C. Polyurethane and Modified Systems

A series of polyurethane elastomers, both prepolymers and non-prepolymers, were studied as prime adhesive constituents and also as modifiers for epoxy and polyamine based adhesive systems. Several commercial polyurethane adhesives were included in the evaluation.

First, Adiprene L polyurethane prepolymer was used as the prime adhesive and cured at room temperature and contact pressure with two latent amine catalysts, Moca and MDA (methylene dianiline). The Adiprene L/Moca system gave the highest tee peel strength at -320°F of any adhesive evaluated in this program; namely,

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TABLE 24

STUDIES WITH POLYURETHANE PREPOLYMER AS STRUCTURAL ADHESIVES
FOR VERY LOW-TEMPERATURE APPLICATION

Code	Prepolymer	Prepolymer Free Isocyanate, %	Curing Agent	Curing Conditions	Tensile Shear, psi*		Tee Peel, lbs/1"**	
					R.T.	-320°F	R.T.	-320°F
AD	Polycaprolactone 1800-MDI	14.0	TP 440	Autoclave 250°F, 1 hr	3900	6167***	35.0	12.5
AH	" 3,400-MDI	"	"	"	1708	5432***	25.0	6.0
AK	" 10,000-MDI	"	"	"	2282	5038****	21.0	11.0
AM	" 20,000-MDI	"	"	"	3133	5147***	30.0	10.0
AA	" 1,800-MDI	"	Moca	"	1745	5230***	10.0	9.0
AE	" 3,400-MDI	"	"	"	288	4365	2.5	7.5
U	" 1,800-MDI	"	"	"	3313	2100	15.0	6.0
V	" 3,400-MDI	"	"	"	2268	964	25.0	1.0
AC	" 1,800-MDI	"	TMP	250°F, 1 hr Autoclave	1749	3252	12.5	13.0
AG	" 3,400-MDI	"	"	"	2520	3495	7.5	5.0
AL	" 10,000-MDI	"	"	"	2105	2070	5.0	4.0
AO	" 10,000-MDI	"	TEG	"	338	1375	5.0	0.0
AY	TP 740-MDI	5.0	TP 440	"	4343	5257***	22.5	12.5
BD	TP 740-MDI	"	TP 740	"	3153	5456***	43.0	12.5
AQ	Polycaprolactone-Propylene Oxide-MDI***	14.0	TP 740	"	2090	4803	25.0	6.0
AP	"	"	"	"	666	1787	10.0	4.0
AZ	TP 740-MDI	5.0	"	R.T.	1364	3470	35.0	5.0
BB	LHT 240-MDI	"	LHT 240	R.T.	274	922	7.5	0.5

*   Average of four specimens
**   Single specimens
*** Metal failure
**** 2 to 1 mole ratio of polycaprolactone to propylene oxide

TEG - Triethyleneglycol
MDI - Methylene bis(phenyl-4-isocyanate)
TMP - Trimethylol propane

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TABLE 25

STUDIES WITH NON-PREPOLYMER POLYURETHANES AS STRUCTURAL ADHESIVES FOR VERY LOW-TEMPERATURE APPLICATION

Code	System	Cure	Tensile Shear***, psi		Tee Peel****, lbs/1"	
			R.T.	-320°F	R.T.	-320°F
AU	TDI TP-440	Autoclave 250°F	4953	5197**	4.0	5.0
AV	TDI TP-740	"	1265	5237**	17.5	10.0
AW	MDI TP-740	"	2693	5287**	35.0	15.0
AX	MDI LHT-240	"	3180	4377*	32.5	15.0

   * Monomers combined on an equivalent basis

  ** Metal failure

 *** Average of four specimens

**** Single specimens

40.0 lbs/1". The room temperature properties were only mediocre, but it was anticipated that incorporation of RT-curing, epoxy-based adhesives would overcome this difficulty.

Secondly, three commercial polyurethane prepolymer adhesives were obtained and evaluated to further explore the low temperature potential of this family of adhesives. Bonding difficulty resulted in curing these at room temperature because of the long time required to dry the solvent. Exposure of the free-isocyanate-containing prepolymer to moisture in the atmosphere resulted in a blowout of the bonds during cure. The low temperature strengths were not very interesting.

Finally, Adiprene C, a polyurethane rubber and non-prepolymer, was used to modify epoxy polyamide adhesives. The urethane was dissolved in the epoxy constituent by heating and, finally, this was combined with the polyamide. The epoxy to polyamide ratio was maintained at 1/1, but the urethane level was varied from about 16 to 150 phr per combined parts of epoxy-polyamide. No attempts were made to crosslink the polyurethane; the epoxy-polyamide was cured at RT as well as 250°F. The strength levels were not very promising and further work was discontinued.

Table 26 shows the results of this work and emphasizes the tremendous potential of the amine-cured polyurethane prepolymers at extremely low temperature, particularly of the peel strength.

Because of the excellent results attained with Adiprene L-100, several other commercially available polyurethane prepolymers were evaluated at very low temperature. These included Adiprenes LD-167, LD-213, and LM-52. The percentage-free isocyanates are 9.5, 6.6, and 9.5, respectively. Cure was accomplished at ambient temperature with Moca.

Table 26 shows the results of this study. Code #233 appears to cure faster than Adiprene L-100, developing higher RT and -320°F shear and tee peel strength in shorter time. On this basis it could be suggested as a replacement for Adhesive C.

Replacements for the amine curing agent, Moca, in urethane elastomer adhesives were tried in an attempt to hasten the cure time for this system and at the same time improve the ambient and elevated temperature physical properties. Adiprenes L-100, L-167, and L-213 were selected as the urethane elastomers, and DMP-10 as the amine curing agent. Table 26, Code Numbers 263, 266, and 267, reveals the results of this work. Results were not sufficiently rewarding to further consider this approach.

A new polyurethane elastomer, Estane, reported to be a true thermoplastic requiring no cure or crosslinking, was obtained and evaluated as a hot-melt adhesive at extremely low temperature. The thermoplastic was pressed to a 10-mil film under heat and pressure. The resultant film was inserted between 7075-T6 adherends and pressed 15 minutes at 350°F and about 25 psi, followed by cooling to ambient temperature under pressure. As shown in Table 26, the tee peel strengths at -320°F were not as good as those of previous polyurethanes.

TABLE 26

POLYURETHANE AND MODIFIED SYSTEMS

Code	Adhesive System (weight ratios)	Cure, Days @ RT	Tensile Shear, psi*		Tee Peel, lbs/1"**	
			R.T.	-320°F	R.T.	-320°F
P	Adiprene L-100 Moca, 100/11	1 Hr at 250°F	634	1574	15.0	2.5
185	Adiprene L-100/Moca, 100/11 (Adhesive C)	5 - 9	1670	5157	22.5	40.0
186	Adiprene L-100 MDA, 100/8.2	5 - 9	943	5277	25.0	35.0
182	Multron R12/Mondur CB 75, 100/120	10 - 14	1649	2175	12.5	4.0
184	Multranil 176/Mondur CB75, 100/5	10 - 14	1280	4085	10.0	5.0
180	Multron R12/Mondur CB75, 50/50	4	720	2005	6.0	2.5
			Bonds badly blown			
145	Adiprene C/Versamid 125/Epon 828, 25/75 75	1 Hr at 250°F	5135	2910	5.0	4.0
146	Adiprene C/Versamid 125/Epon 828, 50/50 50	1 Hr at 250°F	3895	2442	7.5	4.0
147	Adiprene C/Versamid 125/Epon 828, 75/25/25	1 Hr at 250°F	147	1818	10.0	4.0
148	Adiprene C/Versamid 125/Epon 828, 25/75/75	13	3570	1500	5.0	2.5
149	Adiprene C/Versamid 125/Epon 828, 50/50/50	13	3030	1534	10.0	2.5
232	LM-52 100 parts Moca 25 phr	7 - 8	230	714	9.5	1.5

233	Adiprene
	  LD-167 100 parts
	Moca 20 phr
	  (Adhesive D)
		7 - 8	2160	4848	27.0	32.5

234	Adiprene LD-213 100 parts Moca 25 phr	7 - 8	3725	2495	27.5	10.0
263	Adiprene L-100, DMP-10, 8 phr	4 - 5	385	2415	6.0	5.0
266	Adiprene L-167, DMP-10, 8 phr	4 - 5	262	1733	5.0	11.0
267	Adiprene L-213, DMP-10, 10 phr	4 - 5	245	2525	13.0	10.0
275	Adiprene L-213, 30 pbw Epon 812 40 Epon 828 30 Shell Z 20	4	4332	1679	1.0	1.5

* Average of 4 specimens

** Single specimens

TABLE 26 (Continued)

Code	Adhesive System (weight ratios)	Cure, Days @ RT	Tensile Shear, psi*		Tee Peel, lbs/1"**	
			R.T.	-320°F	R.T.	-320°F
297	Estane 5740x1	15 Min. @ 350°F	1453	4835	25.0	11.0
298	Estane 5740x2	15 Min. @ 350°F	843	5010	16.0	9.0
351	HMDI/LM-52, 5% free NCO, Moca 14 phr	4	93	1019	0	0
352	HMDI/PP2025, 5% free NCO, Moca 14 phr	4	40.5	697	0	0

* Average of 4 specimens

** Single specimens

Some of the new aliphatic isocyanate (hexamethylene diisocyanate) was obtained and reacted with a diol and also a triol to yield polymers with a 5% free isocyanate content. Curing was attempted with Moca. Although the viscosity increased appreciably, indicating reaction, there apparently were not sufficient functions to produce a polymer suitable as an adhesive. It was anticipated that the linear nature of these polymers would be an asset in the cryogenic regions. The resulting data are shown in Table 26.

D. Selection of Adhesive C

The adhesive consisting of Adiprene L-100 polyurethane elastomer cured at RT and contact pressure with 11 phr Moca (referred to in Table 26, Code #185) was selected for further evaluation and study in view of its ease of processability and superior strength and toughness at very low temperature. This system was designated, Adhesive C.

E. Selection of Adhesive D

The adhesive consisting of Adiprene LD-167 polyurethane elastomer cured at RT and contact pressure with 20 phr Moca (referred to in Table 26, Code #233) was selected for further evaluation and study in view of its ease of processability, faster curing characteristics as compared with Adhesive C, and very acceptable strength and toughness at very low temperature. This system was designated Adhesive D.

XVI. STUDY OF FABRIC SUPPORTED ADHESIVE SYSTEMS FOR APPLICATION AT VERY LOW TEMPERATURE

It is a well-established fact that supporting carrier fabrics can contribute adhesive toughness to many adhesive systems, as evidenced by improved peel strength. It was anticipated that the good low-temperature tee peel strength of Adhesive C might be improved even further by such a tehcnique. A tight-weave glass fabric (181 - 112) and an open-weave, nylon-marquisette fabric were coated with the adhesive and interposed between coated faying surfaces of test specimens. Cure was accomplished at RT and contact pressure. The resulting data are shown in Table 27, Code 272 and 273.

Carrier fabrics tended to significantly upgrade tee peel strength, or adhesive toughness, of a polyurethane adhesive at extremely low temperature. A tee peel strength in excess of 60.0 lbs/1" at -320°F was achieved with a tight-weave glass fabric and Adhesive C, the highest value obtained with any adhesive to date.

Because of the very excellent peel strength at -320°F demonstrated by 181-112 carrier fabric when employed with a polyurethane elastomer (Adhesive C), it was decided to study the effects of a number of other carrier fabrics.

HG-32 glass skrim cloth, 104-Volan A glass fabric, nylon parachute fabric, unbleached cotton muslin, and a nonwoven dacron mat pressed onto a cotton skrim (Webril 1514-M) were selected. Bonds were made using Adhesive C. The adhesive was 7-75-T6 adherend. Curing was accomplished at RT and contact pressure.

Table 27 shows the resultant data. None of the carriers screened produced as high a peel strength at -320°F as the 181-112 glass fabric previously reported.

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TABLE 27

STUDY OF FABRIC SUPPORTED ADHESIVE SYSTEMS
FOR APPLICATION AT VERY LOW TEMPERATURE

Code No.	Adhesive	Cure, Days @ RT	Tensile Shear Strength, psi		Tee Peel Strength, lbs/1"	
			-320°F	R T.	-320°F	R.T.
272	ADHESIVE C plus 181-112 Glass Fabric Carrier(Adhesive E)	8	4890*	1139	60.0*	33.2
273	ADHESIVE C plus Nylon Marquisette Fabric Carrier	8	5252*	851	53.0	17.5
299	ADHESIVE C + 112-112 Carrier	2	1447	5095*	27.0	26.0
292	Same as #299, except HG-32 glass carrier	2	1278	5110*	31.0	36.0
293	Same as #299, except 104-Volan A carrier	2	1718	5215*	24.0	24.0
294	Same as #299, except nylon parachute carrier	2	1216	5142*	12.1	10.8
295	Same as #299, except cotton muslin, unbleached	2	1068	5440*	20.0	15.0
296	Same as #299, except Webril 1514-M Cotton/Dacron	2	1272	5335*	30.5	17.9

* Failure in adherends

A. Selection of Adhesive E

The adhesive consisting of Adiprene L-100, cured at RT and contact pressure with 11 phr Moca and trowelled onto one layer of 181-112 glass fabric (referred to in Table 27, Code #272), was selected for further evaluation and study in view of its superior toughness at extremely low temperature. This system was designated Adhesive E.

XVII. EVALUATION OF TEFLON FEP AS A HOT-MELT LOX COMPATIBLE ADHESIVE FOR VERY LOW TEMPERATURE APPLICATION

Teflon FEP has already been evaluated as a hot melt adhesive at very low temperature (see Table 21, Code #79). This evaluation was carried out on 7075-T6 aluminum, and although this alloy is not compatible with the high temperature required for bonding, it did establish the utility of this material for very low-temperature adhesive application. More extensive evaluation was made on this alloy; however, it was finally decided to include stainless alloy. These evaluations are treated in subsequent sections.

To attain the uniform high temperatures required for bonding stainless steel, the resistance heating apparatus shown in Figure 22 was designed. This technique could be considered practical for field application. Another heating technique practical for field application could be Narmco's Exotherm bonding.

Various other fluorocarbon films were evaluated as hot-melt adhesives, including Aclar (fluorohalocarbon), PVF (polyvinyl fluoride), Kynar (vinylidene fluoride), and Kel-F (chlorotrifluoroethylene). Teflon FEP and Aclar proved to be processable as adhesives by this technique.

A. Selection of Adhesive F

The adhesive consisting of Teflon FEP(referred to above and processed at 700°F as a hot-melt adhesive)was selected for further evaluation and study because of its LOX compatibility and interesting adhesive properties at extremely low temperature. This system was designated Adhesive F.

XVIII. A STUDY OF VARIOUS CHEMICAL AND PHYSICAL TECHNIQUES FOR IMPROVING THE PROPERTIES OF RT-CURED ADHESIVES AT VERY LOW TEMPERATURE

A. Chemical Accelerators

An attempt was made to impart a more complete cure and faster curing rate in epoxy polyamide systems by using amine salts(15). It was anticipated that greater adhesive strength could be obtained in shorter times, and that a more complete cure would increase the elevated temperature adhesive strength. Shell D polyamine salt was the accelerator selected. It was used at loading rates of 1, 3, and 5 parts per hundred parts of Adhesive A. Table 28 shows the results of this study. A slight improvement was noted in RT tensile shear strength for all loading rates. The -320°F shear strength was not as, but a slight improvement was noted in the 180°F shear strength at a loading rate of 1 phr. Tee peel strength was relatively unchanged. No outstanding advantages could be seen for the use of this accelerator for epoxy polyamide adhesives.
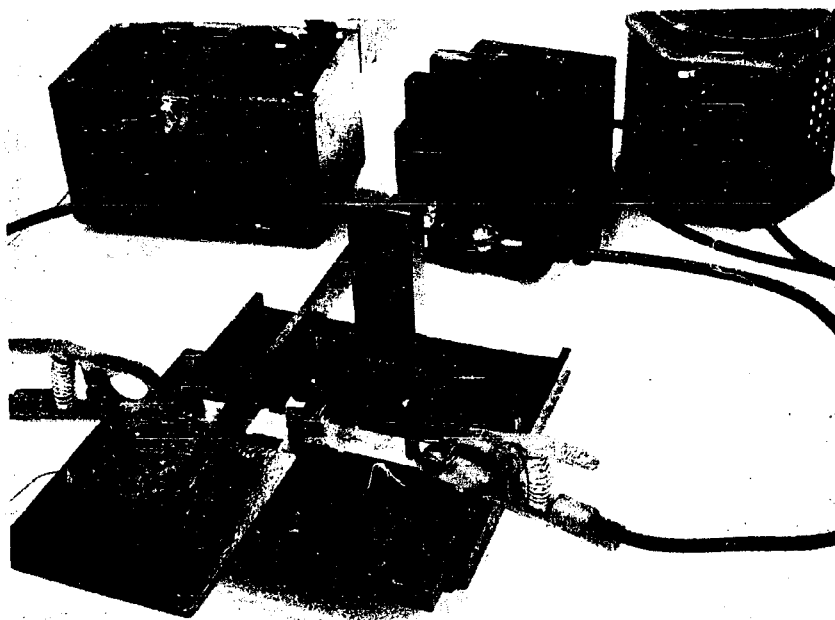
Figure 22. Lab setup for producing bonds with
ADHESIVE F (Teflon FEP) by resistance
heating. This system could be adapted
to field application. Shown are input
powerstat, step-down transformer (5V-
115A), potentiometer, curing jig, and
stainless steel adherends being bonded.
Note shunt bars around the 1/2" over-
lap area.

TABLE 28

A STUDY OF VARIOUS CHEMICAL AND PHYSICAL TECHNIQUES FOR
IMPROVING THE PROPERTIES OF RT-CURED ADHESIVES AT VERY LOW TEMPERATURES

Chemical Accelerators

Code	Test Condition	Cure at R.T.	Tensile Shear, psi	Tee Peel, lbs/1"
206	Adhesive A + 1 phr Shell D accelerator			
	-320°F	7 days	2802	3.4
	R.T.	7 days	3522	4.0
	+125°F	7 days	1792	---
	+180°F	7 days	618	---
207	Same as 206, except 3 phr			
	-320°F	7 days	1787	3.5
	R.T.	7 days	3365	3.0
	+125°F	7 days	1424	---
	+180°F	7 days	453	---
208	Same as 206, except 5 phr			
	-320°F	7 days	2010	3.75
	R.T.	7 days	3402	4.0
	+125°F	7 days	1489	---
	+180°F	7 days	453	---

Ultrasonic Energy

Specimens	RT Tensile Shear Strength, psi
Control #1 16 Hour Cure at 75°F	2570
Control #2 1 Hour Cure at 150°F	4440
16 Hours Cure at 110°F with 54 KC ultrasonic input (enveloped in polyethylene bag)	3290
16 Hours Cure at 110°F with 54 KC Ultrasonic input (not enveloped in a bag)	1520

TABLE 28 (Continued)

Code No.	Adhesive	Cure, Days @ RT	Tensile Shear Strength, psi		Tee Peel Strength, lbs/1"	
			-320°F	R T.	-320°F	R.T.
	Electrical Potential					
---	Resin 3135 & Curing Agent 7111 plus HG-32 glass skrim cloth carrier CONTROL #1	4	2942 (2580-3480)	----	----	----
---	Same as above, except 700 volt AC potential applied across joint	1	3533 (3090-4100)	----	----	----
---	Same as above	4	3205 (3060-3680)	----	----	----
---	Resin 3135 & Curing Agent 7111 plus HG-32 glass skrim cloth carrier, CONTROL #2	1	2250 (820-3040)	----	----	----
---	Same as above, except 510 volt DC potential applied across joint	1	919 (780-984)	----	----	----
	Evaluation of Primes					
300	ADHESIVE A with epoxy-polyamide prime	5	3120	2335	4.5	5.0
301	ADHESIVE B with epoxy-polyamide prime	5	1996	3985	6.0	13.0
302	ADHESIVE C with poly-urethane prime	5	1552	4918	18.0	30.0
	Non-Premixed Two-Part Adhesives					
262	Resin 3135 with Curing Agent 7111, 50/50 pbw.	7 - 8	610	244	2.0	2.5

B. Ultrasonic Energy

Because the targets for this work called for curing adhesives at ambient temperature, it was thought that thermal energy might possibly be replaced with other such forms of energy as ultrasonic, irradiation with ultraviolet light, chemical accelerators, etc. Sonic energy was chosen for study in curing the Resin 3135/7111 adhesive system. The ultrasonic generator was a Model UG140, Serial 20044 made by the Ultrasonics Corporation, and capable of delivering 54 KC energy. This was employed with a Model UT 15S, Serial 1098 tank. Half=inch overlap bonds were made with the above adhesive. One set was enveloped in a polyethylene bag before inserting in the curing fixture, and the other set inserted in a curing fixture with no envelopment. The assemblies were placed in the test tank which was filled with water. The bonds were cured for 16 hours at resonant frequency (54 KC) and a temperature of 110°F. Although a temperature of 75°F was desired, the ultrasonic input caused the temperature to rise. The bond which was not enveloped in polyethylene bag was somewhat damaged by the energy, causing flash of the glueline to emulsify.

Two control bonds were made with the same adhesive for comparison, one being cured 16 hours at ambient temperature in the atmosphere, and the other cured 1 hour at 150°F in an oven. Table 28 shows the results of this study. The data are not conclusive and it was not known whether sonic energy would be of any value in curing. As pointed out, some means would have to be taken to eliminate the effect of thermal energy resulting from ultrasonic energy.

C. Electrical Potential

Several experiments were conducted employing noninductive electrical energy where absolutely no thermal energy was added to the system. One such experiment involved the cure of an epoxy polyamide-adhesive (Resin 3135 and Curing Agent 7111). Standard breakaway panels of 7075-T6 bare aluminum alloy were coated with the adhesive, followed by inserting in the glueline one layer of a glass skrim cloth carrier trowelled with the adhesive. The bonds were then assembled with 1/2" overlap. A 700-volt AC potential was then applied across the joint during the cure. The assembly was similar to a capacitor.

In another experiment, a 510-volt DC potential was applied across the joint of a similar assembly during the cure. Again, absolutely no thermal energy was applied to the system.

Table 28 shows the results of this study. A minor strength advantage (200 psi) could be attained with the 700-volt AC potential. The 510-volt DC potential resulted in an electrolytic action with resultant gas evaluation or "blowing" and reduced bond strength.

D. Ultraviolet Irradiation

An epoxy polyamide adhesive (Resin 3135/7111) was selected as the subject for ultraviolet irradiation. Although not practical for general adhesive bonding where adherends would screen-out such irradiation, the knowledge of radiation affect on this resin was considered desirable. Gel time at constant temperature was the test criteria.

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The resin sample exposed continuously to ultraviolet light without any screen gelled in 35 minutes at 25°C. The sample receiving no irradiation gelled in 90 minutes at the same temperature. The ultraviolet light was a very effective means for hastening the cross linking of an epoxy polyamide adhesive.

E. Magnetic Fields

The effect of magnetic fields on the reactivity and orientation of the enzyme trypsin has been recently reported (16). Application to an epoxy-polyamide adhesive (Resin 3135/7111) was considered worthy, particularly if increased reactivity or a more-than-random orientation of molecules would result and thereby enhance the physical properties of the cured copolymer.

Half-inch overlap joints were prepared with the above adhesive by curing between a close gap of a permanent magnet having a field strength of 1800 gauss. The same procedure was followed utilizing an electro magnet with an AC input. When compared with control bonds employing no magnetic field, no increase in bond strength could be ascertained using this technique.

Because of the very weak electrostatic charges on the epoxy and polyamide molecules a stronger magnetic field probably would be necessary —— in the order of 15,000-50,000 gauss. Obviously, there is a specific magnetic susceptibility for these molecules, and it would only be necessary to employ a sufficiently strong driving force to activate them.

F. Technique for Adhering Plastic Materials

A recent article briefly describes a method of bonding metals to thermoplastic materials with a single layer of molecules as an adhesive. The resulting bond is said to be more resistant to tearing and pulling than is the plastic itself. Such a technique would be a great advantage in this work as it would allow easier bonding of materials such as Teflon to metal adherends. Advantages might be gained in composite bonding. With the sketchy information available in the referenced article (17), the technique was tried.

The technique consisted of forming a monomolecular layer of a long chain hydrocarbon acid, such as stearic acid, on water from a benzene solution. After evaporation of solvent, the acid end of the molecule has an affinity for water and remains in contact with the water surface. The hydrocarbon end has no such affinity and remains clear of the water surface. Compressing the monomolecular layer causes a more positive orientation. Inserting a metallic adherend under the layer causes the acid ends to be deposited on the metal. Making a hot-melt bond with a thermoplastic (such as polyethylene) between adherends treated in this manner, causes the stearic acid to form a chemical aluminum stearate bond with the metal. The hydrocarbon end becomes entwined in the thermoplastic during the fusion process.

Successful bonding was not accomplished, probably because all of the details in forming the monomolecular layer were not understood. The method, although not exactly adaptable to field application, appears to have considerable potential.

G. Evaluation of Primes

The use of prime solutions are well recognized in the art of adhesive bonding for improving adhesive strength. The function of such primes is to cause better wetting of bonding surfaces by the adhesive. It was thought that such a technique might be advantageous for cryogenic applications, particularly where the adhesive must be processed at ambient temperature and wetting might be a direct function of high viscosity.

The developed Adhesives A, B, and C were evaluated at very low temperature with primes. Adhesive A and B were employed with a 10% epoxy-polyamide prime, and Adhesive C with a 10% polyurethane prime —— all cut with toluene. The formulas are shown below:

Epoxy-polyamide Prime		Polyurethane Prime	
Resin 3135	50 pbw	Adiprene L-100	100 pbw
Curing Agent 7111	50 pbw	Moca	11 pbw
Toluene to make 10% solids		Toluene to make 10% solids	

Cleaned 7075-T6 adherends were given one brush coat of prime and immediately transferred to a vacuum chamber and dried one hour at 30" Hg at ambient temperature to remove all toluene solvent. Subsequently, bonding with each of the three adhesives followed standard, established procedures.

Table 28 shows the results of this study. There tended to be a marginal improvement through the use of primes. Peel strength improvement was more pronounced.

H. Non-Premixed Two-Part Adhesives

For the sake of ease of application, it was thought worthwhile to determine what bond strengths could be attained without premixing a two-part adhesive such as an epoxy polyamine. Tensile shear and tee peel specimens were prepared by troweling an even coating of Resin 3135 (epoxy constituent) on one faying surface, and troweling an even coating of Curing Agent 7111 (polyamine constituent) on the other faying surface. The bonds were then made by assembling the adherends coated with the reactive components and applying contact pressure and curing at ambient temperature. Table 28 (Code #262) shows the results of this study. It was concluded that premixing was required to obtain optimum adhesive properties.

I. Simplification of Bonding

The application requirements for this research called for simplification of bonding procedures. The experimental adhesives have been selected with this in mind. We have studied simplified surface preparations such as sandblasting, and satisfied the requirements for bonding at contact pressure and room temperature. Accordingly, it is believed that the best adhesive systems developed to date lend themselves to field application.

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Two adhesive systems have performed very well at very low temperature and at the same time have satisfied the requirements listed above. These are Adhesive A and Adhesive B. Table 29 and Figures 23 and 24 show the results of a study intended to compare the strength of bonds made with these two promising adhesives and cured at RT, 100, 150, and 200°F. Bonds were made by employing the simplest techniques: sandblast and sanding surface preparations, contact pressure, and low curing temperature.

Results indicate that the RT and -320°F tensile shear strength of the nylon-filled system tends to improve slightly with an elevated temperature cure. The RT and -320°F tee peel strength, however, tends to fall off. In the composite system, the RT and -320°F tensile shear strength tend to increase with elevated temperature cure, the -320°F strength showing the greater increase. Although not conclusive, the RT and -320°F tee peel strength of this system showed a tendency to increase with an elevated temperature cure.

XIX. STUDY OF LOX IMPACT INSENSITIVE ADHESIVE SYSTEMS

NASA has performed LOX compatibility tests on some of the developed adhesives and adhesive constituents. The polyurethane elastomer (Adhesive C) proved to be particularly LOX sensitive. The epoxy-polyamide adhesive Resin 3135 and Curing Agent 7111, common to both Adhesives A and B, also proved to be LOX sensitive.

Because Adhesive B contains Teflon, a LOX compatible material, it was decided to evaluate this adhesive in a very special manner. LOX impact testing of polymers is usually conducted on a specimen 11/16" OD x .050" thickness. It was believed that the mass of such a specimen was not truly representative of a glueline 0.005 - 0.008" thickness that would ultimately be required to pass a LOX test. A specimen was designed that more closely represented such a glueline.

Parallel-laminated specimens were prepared by bonding two skins of 0.020" 7075-T6 bare aluminum alloy with Adhesive B, the skins forming the flat outer sides of the specimens with the 5-8 mil glueline between and parallel to the skins. The resultant thickness was about 0.050", and the specimen was formed by cutting to 11/16" OD.

Cross-laminated specimens were prepared by laminating 1" wide x 12" long x .020" strips of 7075-T6 bare aluminum alloy with Adhesive B in such a manner that a 1" x 1" bar stock 12" long resulted. This was turned on a lathe to 11/16" OD from which 50-mil thick specimens were cut. The types of specimens are shown in Figure 25.

NASA reported that the specimens consisting of alternate layers of 7075-T6 aluminum and Adhesive B were somewhat less LOX impact sensitive than the specimens of Adhesive B tested without the aluminum adherend. The reduction in impact sensitivity of Adhesive B was attributed to energy absorption by the aluminum adherend. Somewhat variable results were obtained in these tests, however.

Further testing of adhesives was performed without adherends of any kind. Heterogeneous adhesives for LOX applications required separate testing for each constituent.

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TABLE 29

SIMPLIFICATION OF BONDING

Adhesive System	Curing Conditions	Tensile Shear, psi		Tee Peel, lbs/1"	
		R.T.	-320°F	R.T.	-320°F
Resin 3135 (epoxy-polyamide filled with 33.3 phr 200-mesh powdered nylon (Zytel 61)	14 Days @ RT	3020	2085	5.0	5.0
	1 Hr. @ 100°F	3070	2920	5.0	5.0
	1 Hr. @ 150°F	3145	3220	5.0	5.0
	1 Hr. @ 200°F	3540	3370	4.0	4.0
Two substrate films of 1-mil Teflon FEP with Na-naphthaline etch bonded with Resin 3135 (epoxy-	6 Days @ RT	1590	3345	4.0	12.5
	1 Hr. @ 100°F	1859	3110	5.0	20.0
	1 Hr. @ 150°F	2035	3857	2.5	10.0
	1 Hr. @ 200°F	2113	4845	5.0	15.0

Note: See Figures 23 and 24.
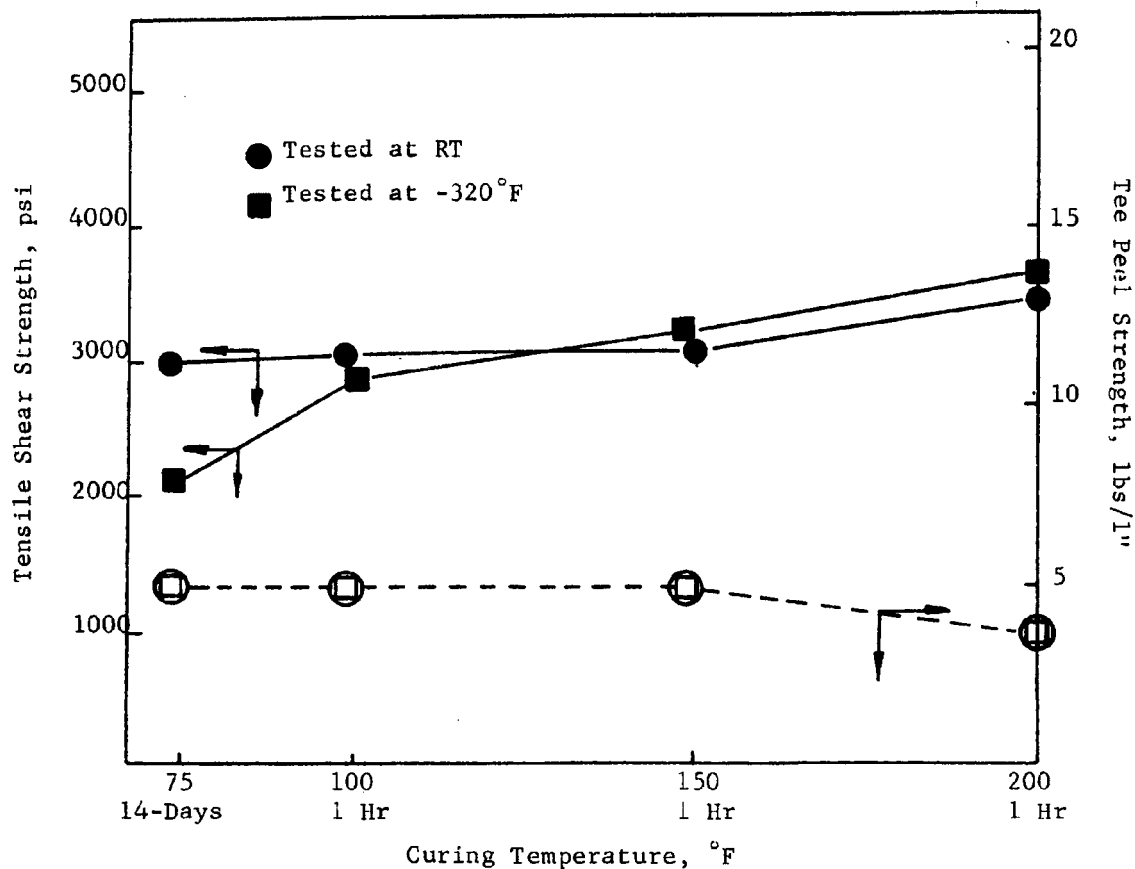
Figure 23. Simplification of bonding procedures --

The effect of curing temperature on the bond
strengths of Resin 3135 (epoxy-polyamide) filled
with 33.3 phr powdered nylon (Zytel 61).

Tensile shear specimens were given a sandblasted surface treatment.
Average of 4 specimens.

Tee peel specimens were given an abraded surface treatment (W 400A Soft-
Back wet-or-dry abrasive paper). Single specimens.
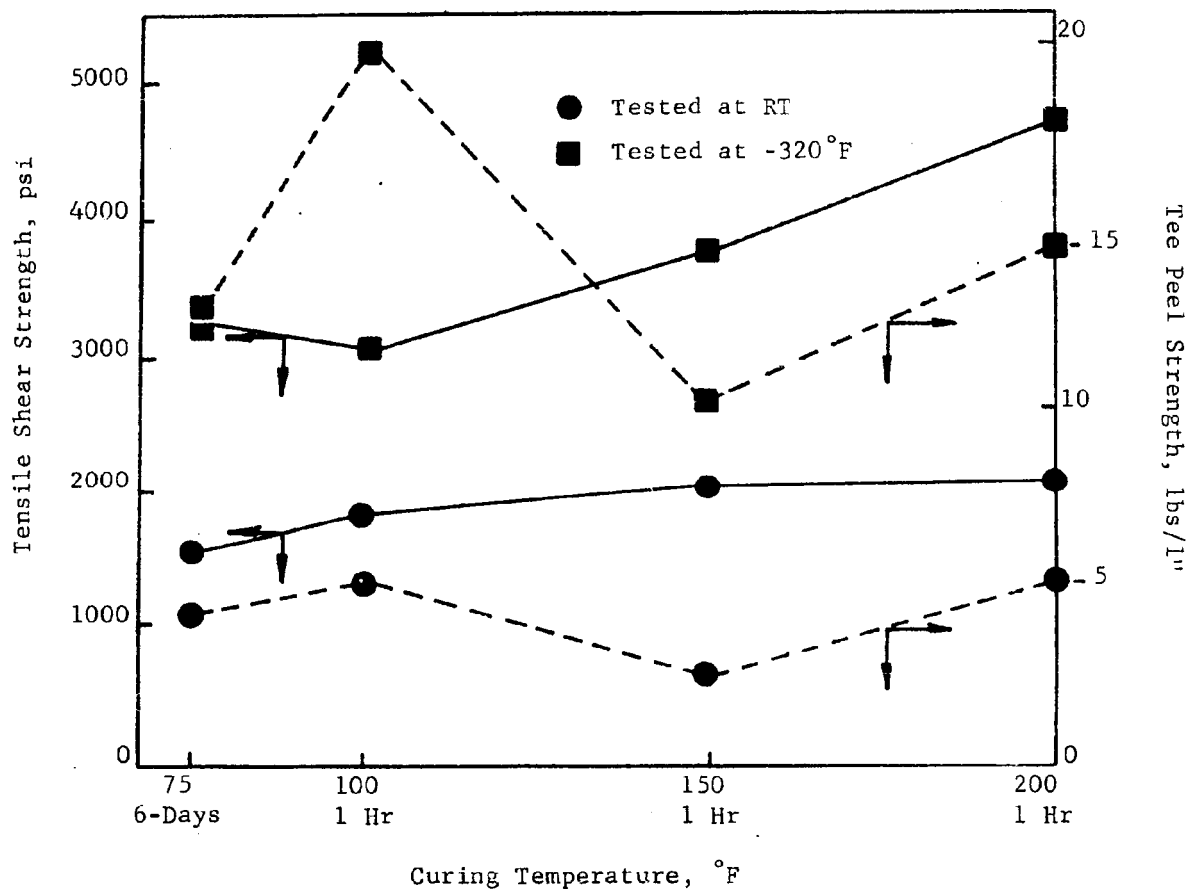
Figure 24.   Simplification of bonding procedures --

The effect of curing temperature on the bond
strength of a composite adhesive consisting
of two substrate films of 1-Mil Teflon FEP
with sodium-naphthalene etch bonded with Resin
3135 (epoxy-polyamide).

Tensile shear specimens were given a sandblasted surface treatment.
Average of 4 specimens.

Tee peel specimens were given an abraded surface treatment (W 400A,
Soft-Back wet-or-dry abrasive paper).   Single specimens.

Figure 25. Illustrating LOX compatibility specimens
prepared with ADHESIVE B (composite sys-
tem consisting of Teflon FEP films in an
epoxy-polyamide). Parallel-laminated and
cross-laminated specimens were made using
20-mil 7075-T6 aluminum. Specimen dimen-
sions were 11/16" OD x .050".

Any adhesive consisting of a LOX sensitive constituent was considered LOX sensitive. Because of the extreme hazard and the consequent stringent safety requirements involved, such compounds could not be used in launch vehicle LOX 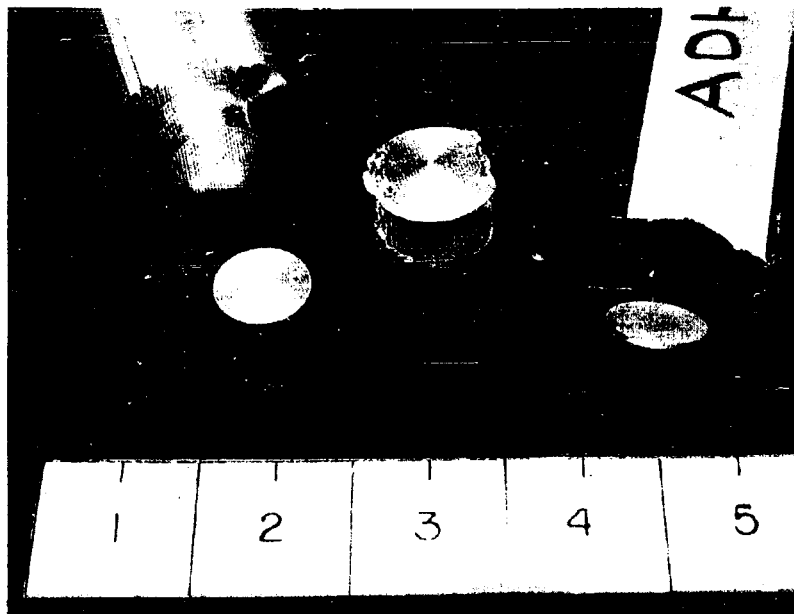systems, even though a specific design application might partially or wholly shield the sensitive component. There is always the possibility that the sensitive component can become exposed to direct impact in LOX, and this situation, however remote, can only be avoided if such materials are not used.

The indicated sensitivity of organic materials to LOX impact critically limits the selection of adhesive constituents to a very few materials which exhibit adhesion ── polytetrafluorethylene, polychlorotrifluorcethylene, and a copolymer of hexafluoropropylene and vinylidene fluoride ── all halogenated high polymers. Usually, processing can only be accomplished under the most rigorous conditions.

A search of the literature revealed great discrepancies between which materials are LOX impact sensitive and insensitive. One report revealed that many polymers previously reported as LOX sensitive, were in fact LOX insensitive when employed in a very pure state (18).

The manufacturers of perhalo monomers, more specifically of perfluoro monomers, were contacted throughout the country in an attempt to obtain suitable m monomers for synthesis work. Perfluoro diamines and perfluoro di- and tri-isocyanates were sought. These were intended for the synthesis of perfluoro nylons and polyurethanes for upgrading the LOX impact compatibility and general cryogenic properties of such polymers. The results were negative, and although preparation of such monomers is possible, the program could not justify their preparation. Sources for perfluoro diacyl chlorides, dibasic acids, and diols were found.

Every technique at our disposal was employed for the development of structural adhesives which would prove to be LOX compatible. The method of approach to such adhesives was threefold: (1) utilizing haloplastic films known to be LOX compatible as hot-melt adhesives, (2) formulating existing adhesives with flame retardants and using the ASTM D-635-56T Flammability Test as a criteria, and (3) synthesizing new perhalogenated polymer structures which can be expected to exhibit LOX compatibility.

A. Formulation Studies

A series of inorganic flame retardants (calcium carbonate, antimony trioxide, and barium sulfate) was used at a 33 and 67 phr level to load the epoxy polyamide adhesive Resin 3135. Two commercial organic flame retardants were also included. After curing at RT the resin specimens were subjected to the above flame test. The inorganic agents were not capable of rendering the specimens "non-burning" at the levels studied. On initial ignition there was a tendency for the heterogeneous mass to melt with the resin flowing away from the retardants. In so doing, combustion was supported. It is emphatically pointed out here that this phenomenon may not impair LOX compatibility.

The organic or semi-organic retardants were completely compatible with the resin system, forming a homogeneous mass. At the concentration levels used, these agents were not effective for producing a "non-burning" test result.

Results of the flammability tests are shown in Table 30. It was concluded that at the concentration levels employed, organic and inorganic flame retardants were not effective in rendering this epoxy polyamide resin "non-burning" by this test.

Adhesive bonded specimens were made with the organic flame retarded systems. These results are shown in Table 31. The retarders tend to lower the adhesive strength at RT as well as at -320°F. Greater concentrations probably could not be employed because of the sacrifice to adhesion.

Adhesive studies were also performed on a brominated epoxy resin (Epi-Rez 5163), a chlorinated rubber (Parlon 300), chlorinated polyesters (Hetron 32A and 92) and a chlorinated epoxy (ERL 0625). All of these materials were reported by their manufacturers to pass the ASTM flammability test. The test data are shown in Table 31. The halogenated polymers showed significantly poorer adhesion properties than their nonhalogenated counterparts. Use of such systems could be justified only if LOX compatibility could be assured.

An article (19) indicated the advantages of employing powdered polyfluoro-carbons as fillers for polyurethane elastomer systems. The advantage sought from such practice was to render the system insensitive to impact under liquid oxygen. However, subsequent discussions with the agency performing the tests have revealed that this is not a satisfactory solution to the problem.

Adhesives C and D were modified with 33.3, 67.7, and 100 phr Teflon TFE powder (unetches). Bonds were prepared with the modifications, and the test results are shown in Table 31.

In general, filling Adhesive C and D with Teflon powder resulted in poorer adhesive strength and toughness, both at -320°F and RT, than in the unfilled adhesives.

Approximately one hundred LOX compatibility specimens (.050" x 11/16" OD) for each of the four systems indicated in Table 32 were submitted to NASA for testing. This was an attempt to study the following variables on LOX compatibility:

a. Chlorine contents ranging from approximately 20-50%
b. Polyester vs. epoxy chemical structure
c. Effectiveness of flame retarding agents
d. Correlation of LOX compatibility with ASTM D-635-56T burning test

The test results are shown in Table 32. All specimens were found to be consistently sensitive to LOX. At this point some very definite conclusions were drawn as a guide to the development of LOX compatible structural adhesives. First, chlorination or degree of chlorination, up to 50%, was not effective in producing a LOX compatible test result. Perhaps halogen contents approaching 75-80%, as in cases of Teflon and Kel-F, would be effective, but this would only be possible

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TABLE 30

ADHESIVE FLAMMABILITY STUDIES AS A
GUIDE TO LOX COMPATIBILITY

Code No.	System	Flammability Test per ASTM D-635-56T
---	Resin 3135 plus 33 phr Calcium Carbonate	Burns
---	Resin 3135 plus 67 phr Calcium Carbonate	Burns
---	Resin 3135 plus 33 phr Antimony Trioxide	Burns
---	Resin 3135 plus 67 phr Antimony Trioxide	Burns
---	Resin 3135 plus 33 phr Barium Sulfate	Burns
---	Resin 3135 plus 67 phr Barium Sulfate	Burns
334	Resin 3135 plus 10 phr Phosphorane	Burns
335	Same as #334, except 30 phr	Burns
336	Same as #334, except 50 phr	Burns
333	Resin 3135 plus 30 phr Pyrostop E-100	Burns
337	Same as #333, except 40 phr	Burns
338	Same as #333, except 50 phr	Burns
339	Resin 3135 + 100 phr Teflon 7	Burns
311	ADHESIVE C plus 100 phr Teflon 7	Burns

The organic or semi-organic retardants were completely compatible with the resin system, forming a homogeneous mass. At the concentration levels used, these agents were not effective for producing a "non-burning" test result.

Results of the flammability tests are shown in Table 30. It was concluded that at the concentration levels employed, organic and inorganic flame retardants were not effective in rendering this epoxy polyamide resin "non-burning" by this test.

Adhesive bonded specimens were made with the organic flame retarded systems. These results are shown in Table 31. The retarders tend to lower the adhesive strength at RT as well as at -320°F. Greater concentrations probably could not be employed because of the sacrifice to adhesion.

Adhesive studies were also performed on a brominated epoxy resin (Epi-Rez 516), a chlorinated rubber (Parlon 300), chlorinated polyesters (Hetron 32A and 92) and a chlorinated epoxy (ERL 0625). All of these materials were reported by their manufacturers to pass the ASTM flammability test. The test data are shown in Table 31. The halogenated polymers showed significantly poorer adhesion properties than their nonhalogenated counterparts. Use of such systems could be justified only if LOX compatibility could be assured.

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Adhesives C and D were modified with 33.3, 67.7, and 100 phr Teflon TFE powder (unetches). Bonds were prepared with the modifications, and the test results are shown in Table 31.

In general, filling Adhesive C and D with Teflon powder resulted in poorer adhesive strength and toughness, both at -320°F and RT, than in the unfilled adhesives.

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a. Chlorine contents ranging from approximately 20-50%
b. Polyester vs. epoxy chemical structure
c. Effectiveness of flame retarding agents
d. Correlation of LOX compatibility with ASTM D-635-56T burning test

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TABLE 31

LOX IMPACT FORMULATION STUDIES
(7075-T6 Bare Aluminum)

Code No.	System	RT Cure, days	Tensile Shear, psi		Tee Peel, lbs/1"	
			-320°F	RT	-320°F	RT
315	Epon 812/Epi-Rez 5163, 5/20, 10 phr Shell U	25	217	635	----	----
316	Same as #315, except 30 phr Shell U	25	747	1100	----	----
317	Same as #315, except 50 phr Shell U	25	658	1042	----	----
319	Epon 828/Parlon 300, 100/5,30 phr Shell U	4	699	1141	0.5	0.5
328	Hetron 32-A/MEK peroxide/Co-naphth, 2%/0.5%	6	601	1606	----	----
329	Same as #328, except 5%/1.25%	6	825	1572	----	----
330	Hetron 92/MEK peroxide/Co-naphth, 2%/0.5%	6	473	1059	----	----
331	Same as #330, except 5%/1.25%	6	532	1146	----	----
333	Resin 3135 plus 30 phr Pyrostop E-100	4	1239	3940	----	----
337	Same as #333, except 40 phr	10	1292	2085	----	----
338	Same as #333, except 50 phr	10	1251	2580	----	----
334	Resin 3135 plus 10 phr Phosphorane	4	1426	2292	----	----
335	Same as #334, except 30 phr	10	2165	2932	----	----

TABLE 31 (Continued)

Code No.	System	RT Cure, Days	Tensile Shear, psi		Tee Peel, lbs/1"	
			-320°F	RT	-320°F	RT
336	Same as #334, except 50 phr	10	2432	2747	---	----
340	Hetron 92/MEK peroxide/Co-naphth., 100/2%/0.5% plus two 1-mil substrate films Teflon FEP, Type 544	3	402	1083	2.9	1.9
341	Same as #340, except 33.3 phr Antimony Trioxide	3	633	1470	2.0	0.97
342	ERL 0625/MPDA, 100/10.6	6 hrs @ 325°F	1530	2001	---	----
343	ERL 0625/HET/BDMA 100/145/1/2%	6 hrs @ 325°F	913	1070	---	----
344	Same as #342, except two 1-mil substrates of Teflon FEP, Type 544	6 hrs @ 325°F	4295	1939	3.5	2.3
345	Same as #343, except two 1-mil substrates of Teflon FEP, Type 544	6 hrs @ 325°F	3687	1823	9.1	2.3

LOX IMPACT INSENSITIVE ADHESIVE SYSTEMS
(Hot Melt Bonds)

Code No.	Adhesive System	Fusion Temp.	Test Temp.	Tensile Shear, psi	Tee Peel lbs/1"
---	ADHESIVE F (5-mil Teflon FEP, Type A, film)	700°F	-423°F	5373*	----
			-320°F	4080*	51.0
			-67°F	3190	18.5
			RT	1448	10.0
			+125°F	930	5.5
			+180°F	823	4.5
304	Aclar 22C 5-mil (fluorohalocarbon film)	600°F	-320°F	4214	10.5
			RT	1817	8.9

Tensile Shear Specimens -- 0.050" 17-7 stainless steel 1" wide coupons with hydrogen peroxide etch and nonded with half-inch overlap by resistance heating. Average of 4 specimens. Tested per MIL-A-5090D.

Tee Peel Specimens ------- 0.020" 17-7 stainless steel 1" x 12" coupons with hydrogen peroxide etch and bonded with total overlap by resistance heating. Single specimens. Tested at a head travel of 2"/min.

* Failure in gripping ends of metallic adherends

TABLE 32

COMPATIBILITY OF CHLORINATED RESIN SYSTEMS
WITH LIQUID OXYGEN

LOX Compatibility Specimens	Code No.	System	Flammability Test per ASTM D-635-56T*	Chlorine Analysis, Percent**	Thickness, inch	Impact Energy, ft-lbs ***	No. Reactions/No. Tests ***
#1	340	Hetron 92/MEK peroxide/Co naphthenate, 100/2%/0.5%(chlorinated polyester)	Burns	26.0	.050	72.3	7/10
#2	341	Same as #340, except 33.3 phr antimony trioxide(chlorinated polyester)	Non-burning	20.6	.050	72.3 36.15 21.69 14.60 7.23	9/10 2/10 1/10 2/10 0/20
#3	342	ERL 0625/MPDA, 100/10.6(chlorinated epoxy)	Burns	25.3	.050	72.3 36.15 21.69	7/10 2/10 0/20
#4	343	ERL 0625/HET/BDMA, 100/145/½%	Non-burning	46.5	.050	72.3 36.15 21.69 14.46 7.23	6/10 6/10 2/10 1/10 0/20

* Flammability of Rigid Plastics Over).050" in Thickness

** Parr bomb ignition and Volhard titration

*** Data Provided by NASA, Huntsville

MEK - Methyl ethyl ketone
Co   - Cobalt
MPDA - Metaphenylene diamine
HET - Chlorendic anhydride
BDMA - Benzyl dimethyl amine

with perhalogenation. Resins that could be processed at room temperature as adhesives were not available with such high halogen contents. Addition of halogen as a filler was not promising.

Second, polyester chemical structure could not be differentiated from epoxy chemical structure with respect to LOX compatibility. Third, the use of inorganic flame retardants (such as antimony trioxide) with a highly chlorinated polyester resin was not effective for producing a LOX compatible test result.

Finally, there appeared to be no significant correlation between the burning in air and LOX compatibility.

All of the above LOX specimens were 0.050" thick and 11/16" OD. All were hard and brittle, a factor which would have been in their favor. It has been reported that very brittle materials may shatter beneath the pin too easily to absorb the full impact of the striker. Resilient materials are said to detonate more easily than brittle materials, particularly if thin (20).

Chemical bond energies may explain why Teflon, for example, is LOX safe. The F-C bond energy is 105.4 Kcal/mole, whereas the C-H bond is 98.8, the C-C bond 83.1, and the C-Cl bond 78.5 Kcal/mole. Postulating then, perfluorination (75-80%) may be the only means of attaining LOX compatibility, such as perfluorinated epoxy, polyester, polyurethane, and similar resins.

A small amount of work was done with flame retardants in an attempt to render an epoxy-polyamide adhesive (Resin 3135/7111) "non-burning" by the ASTM test. Dechlorane (5-10 micron) was used at a filler loading level of 33, 67, and 100 parts per one-hundred parts resin. A "non-burning" test result could not be attained at the two lower loading rates, but was attained at the higher level.

Because of the results in the foregoing section, no further work was conducted with flame retardants or burn tests.

B. Synthesis Work

It has already been pointed out that there are no polymers having LOX compatibility which can be processed as room temperature curing adhesives. Synthesis of new polymer structures or modification of existing polymers is the only approach to the desired adhesives having LOX compatibility.

It has been reported (21) that there appears to be a correlation between flammability and LOX compatibility of polymers (i.e., those that burn in air are not LOX safe and those that do not burn in air might possibly be LOX safe). The ASTM D 635-56T flammability test was selected as a screening guide. Several alkyd resins were prepared with a chlorinated dibasic acid (chlorendic anhydride) and polyols of various carbon chain length (ethylene, propylene, butylene, and pentylene glycols). It was anticipated that the flammability of the resulting alkyds could be distinguished and correlation made between atomic weight percentage chlorine and flammability characteristics. Thus it might be possible to determine what chlorine content was required in this alkyd chemical structure to produce a "non-burning" test result.

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Although the atomic weight percentage chlorine in the above synthesized alkyds ranged from about 50 to 44 percent, all flammability tests produced a "non-burning" result. It was concluded that the test was not sufficiently sensitive to distinguish burning characteristics. Actually, the alkyds did burn in the presence of an igniting flame, and melted profusely, but were self-extinguishing when the flame was removed.

The atomic weight percentage fluorine in Teflon is about 78 percent, which is reported to be LOX compatible, whereas the percentage fluorine in vinylidene fluoride polymer is about 53 percent, which is reported to be marginally LOX compatible. Since both of these fluorinated polymers give a "non-burning" result according to the above test, it was finally concluded that this flammability test was poor for screening purposes.

The polyurethane elastomers have proven to be the most attractive of all adhesives at temperatures down to the liquid hydrogen point. Unfortunately, they have also proven to be the most LOX sensitive materials. It was natural then that this structure should become the subject for modification. Because of the LOX compatibility afforded the carbon chain by fluorination, as in the case of Teflon, halogenation was the first step in structural modification of the polyurethanes. Perhalogenation was the ultimate goal.

It has been reported (22) that the phenyl isocyanates can be chlorinated directly. The reaction occurs via carbamyl chlorides and can be forced to polychlorinated phenyl isocyanates.

A stream of dry chlorine gas was passed through a column containing tolylene-2,4 diisocyanate in the presence of intense ultraviolet light for a period of about 4 hours. The resulting product, on cooling to ambient temperature, solidified. About ninety percent of the product distilled over at a boiling range of $155°C$-$159°C$ at 17 mm Hg. A quantitative chlorine analysis (sodium fusion) of this fraction was at least 24.6% Cl. This indicated chlorination of only the aliphatic side chain on the aromatic nucleus. The product was judged to be at least $CHCl_2$ (C_6H_3) $(NCO)_2$ having 29% chlorine, or possibly $CCl_3(C_6H_3)$ $(NCO)_2$ having 38% chlorine. In no case could the perchlorinated isocyanate $CCl_3(C_6Cl_3)$ $(NCO)_2$ with 56% chlorine have resulted.

Adiprene L-100 in carbon tetrachloride was also chlorinated in a manner similar to the foregoing halogenation. The product was finally stripped of solvent and the carbamyl chloride broken by heating under 17 mm Hg at $180°C$. The final product was catalyzed with 11 phr Moca, causing an immediate gellation, precluding bond preparation. No explanation could be given for the increased reactivity of the chlorinated product.

XX. COMPREHENSIVE EVALUATION OF ADHEREND SURFACE PREPARATION FOR OPTIMUM ADHESIVE PROPERTIES AT VERY LOW TEMPERATURE

A. Electro Metal Finishing

A comprehensive study of adherend surface preparations has already been accomplished and reported. Adherends included 7075-T6 bare aluminum alloy and 17-7 PH stainless steel. Treatments for the former included a solvent degrease, sandblast, sodium dichromate sulfuric acid etch, anodizing, and the commercial

treatment Prebond 700. The adhesive selected for evaluation against these surfaces was Metlbond 406, a nylon-epoxy adhesive. Tensile shear strength at -320°F was used as the criteria. It was concluded that the anodized surface for aluminum and the hydrogen peroxide surface for stainless steel were optimum. Sandblasted surfaces were found to be close equivalents to these treatments in this study.

More recently, a newer surface treatment has been evaluated -- electro metal finishing.* This process can remove accurately controlled amounts of metal from surfaces. This surface was evaluated in precisely the same manner as the surfaces described above. The same conclusions drawn above still stand, although the electro metal finishing produced quite an adequate surface. Table 33 shows the results of this work.

B. Effect of Adherend Surface Treatments on the Strength of the Developed Adhesive Systems

Although an abraded or sandblasted surface treatment was recommended as a close equivalent to chemical etches when the 350°F cured Metlbond 406 was evaluated, rather erratic data were collected when an abraded or sandblasted surface was used with the developed RT curing adhesives (Adhesives A, B, and C). This effect was noted both in adhesive strength (tensile shear) and adhesive toughness (tee peel). It was felt that more study along the lines of surface preparation was necessary to resolve this difficulty. It initially appeared that curing temperature might dictate a specific surface treatment for optimum bond strength at low temperature and, similarly, that each specific adhesive property sought, such as tensile shear, tee peel, etc., might require its own surface treatment for optimum properties.

Table 34 and Figure 26 reveal the results of a study wherein the three developed adhesives were evaluated against 7075-T6 bare aluminum alloy having a sandblasted and also a sodium dischromate sulfuric acid etch. Cure was at ambient temperature and contact pressure. Tensile shear strength was determined over the temperature range from -320°F to +180°F. It was found that the chemical etch gave significantly better adhesive strength than the sandblasted surface treatment over the entire temperature range investigated.

A similar study was made of the effects of adherend surface treatments on tee peel strength. The results were even more revealing. A sanded surface was used instead of a sandblasted surface and compared with the chemical etched surface. Some of these adhesive bonds were not considered good for reasons explained in the section under "Composite Adhesives."

C. Adherend Chemical Etches for Field Application

Keeping in mind that a chemical etch appears to be indicated in order to obtain optimum adhesive properties, some work was done to adapt the sodium dichromate sulfuric acid etch for field application. The following etchant was prepared:

Sodium Dichromate	30 Parts by weight
Distilled Water	50 Parts by weight
Conc. Sulfuric Acid	50 Parts by weight
Santocel C	10 Parts by weight

*Electro Process & Engineering Corporation, San Diego 10, California

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TABLE 33

EVALUATION OF ADHEREND SURFACE PREPARATIONS FOR
OPTIMUM ADHESIVE PROPERTIES AT
VERY LOW TEMPERATURE

Surface Preparation	Tensile Shear Strength, psi	
	-320°F	RT
7075-T6 Bare Aluminum Alloy		
Solvent Degrease*	1216	2468
Sandblast*	3660	4040
Sodium Dichromate Sulfuric Acid Etch*	3735	6360
Alodine*	977	3235
Anodize*	4691**	5895
Electro Metal Finishing	4200	4262
17-7 PH Stainless Steel		
Solvent Degrease*	3298	4202
Sandblast*	4690	5008
Phosphate Etch*	2280	4095
Hydrogen Peroxide Etch*	5446**	4125
Prebond 700*	3568	4420
Electro Metal Finishing	3640	3920

Adhesive: Metlbond 406, cured 15 min. at 350°F at 25 psi.
Adherends: .064" Breakaway panels, metal and surface treatment as indicated, and bonded with 1/2" overlap.
Testing: Per MIL-A-5090D. Average of four specimens.

*Data taken from Table 7
**Considered Optimum.

TABLE 34

EFFECT OF ADHEREND SURFACE TREATMENTS ON THE
STRENGTH OF THE DEVELOPED ADHESIVE SYSTEMS

Adhesive	Cure Time At RT, days	Test Temp.	Tensile Shear Strength psi*	
			Sandblasted Surface Treatment	Sodium Dichromate Sulfuric Acid Etch
ADHESIVE A	6-7	-320°F	2570	2380
	6-7	-67°F	2282	3180
	6-7	RT	2520	3355
	6-7	+125°F	908	1538
	6-7	+180°F	398	500
ADHESIVE B	6-7	-320°F	2905	4955
	6-7	-67°F	3420	3550
	6-7	RT	1927	1995
	6-7	+125°F	1352	1332
	6-7	+180°F	513	762
ADHESIVE C	6-7	-320°F	3400	5450
	6-7	-67°F	3165	4765
	6-7	RT	781	1561
	6-7	+125°F	576	742
	6-7	+180°F	389	456

Adherends: .064" 7075-T6 Bare aluminum alloy breakaway panels bonded with
1/2" overlap at ambient temperature and contact pressure.

Testing: Per MIL-A-5090D

*Average of four specimens.

Adherends: .064" 7075-T6 Bare Aluminum Alloy Breakaway
                  Panels with 1/2" Overlap
Cure: RT and Contact Pressure
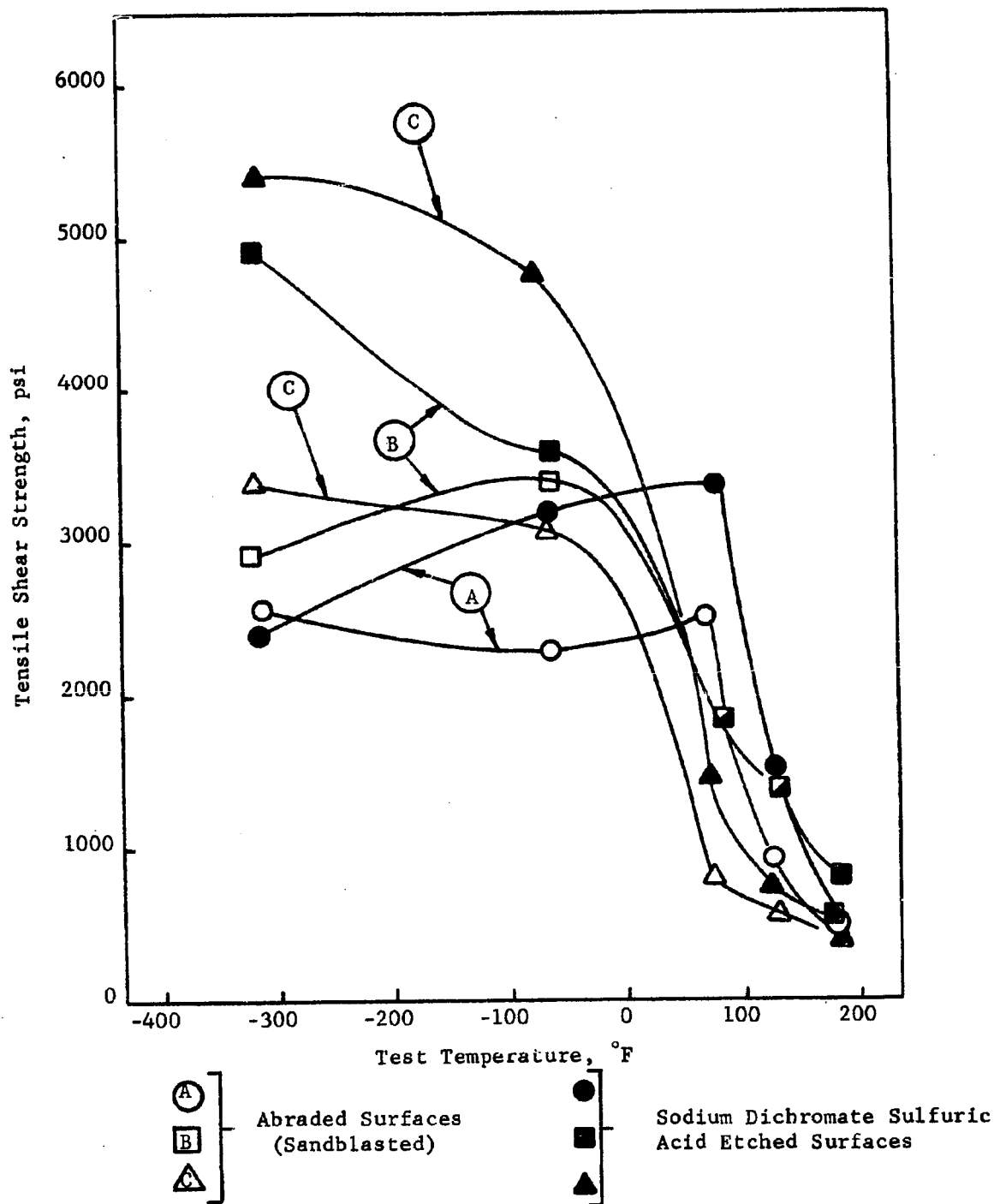Testing: Per MIL-A-5090D

Figure 26. Effect of adherend surface treatment on the
            strength of the developed adhesive systems

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The resultant etchant was a heavy, paste-type material that could be applied to horizontal, vertical, or overhead surfaces with a brush, spatula, or trowel. Surfaces were first degreased with methyl ethyl ketone, coated with the etchant and allowed to remain 50 minutes, then washed down with tap water, and finally air dried. The surface was compared with the standard sodium dichromate sulfuric acid etch described previously. Adhesive C cured at RT contact pressure was used to evaluate the surfaces. Table 35 shows the results of this study.

The paste-type etchant gave excellent tensile shear strength at -320°F; however, all other ambient and low temperature properties were lower than the standard etch. This may have been due to non-optimum curing time at RT.

Some additional work was done in adapting adherend chemical etches for field application. Adhesives A, B, and C were evaluated on 7075-T6 bare aluminum and 17-7 PH stainless steel. The paste-type sodium dichromate sulfuric acid etch, previously described, was used for aluminum. The following paste-type etch for stainless steel was used:

Step #1

Hydrochloric Acid 35%	100	pbw
Hydrogen Peroxide 30%	4	
Formalin 40%	20	
Santocel C	15.5	

Step #2

Sulfuric Acid (conc.)	100	pbw
Sodium Dichromate	10	
Distilled Water	30	
Santocel C (approx.)	15	

The stainless surfaces were treated 40 minutes at RT in Step #1, followed by 40 minutes at RT in Step #2. The results are shown in Table 35. Tensile shear and tee peel strengths were not as good on either adherend with all adhesives as with chemical etches applied at higher temperatures under more controlled conditions.

D. Surface Roughness Studies

Considerable attention has been given to surface roughness in connection with adhesive bonding in recent years. Peel strength (adhesive toughness) has been reported to increase proportionately with degree of surface roughness (23). It was considered worthwhile to study this effect for optimizing adhesive strength and toughness at extremely low temperature.

Five different surface roughness conditions (shown in Table 36) were applied to tensile shear and tee peel adherends. No attempts were made to define the degree of surface roughness, as this would be a very detailed study in itself. Microscopic examination was used to assure that the resulting surfaces had good integrity with no loose particles, and had widely different degrees of roughness. The final treatment was to apply a sodium dichromate sulfuric acid etch to all roughened surfaces to assure that each surface was given the same oxidized surface prior to bonding.

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TABLE 35

CHEMICAL ETCHES FOR FIELD APPLICATION

Chemical Etch and Adhesive	Cure @ RT, Days	Tensile Shear Strength, psi		Tee Peel Strength, lbs/1"	
		-320°F	RT	-320°F	RT
ADHESIVE C with Standard Sodium Dichromate Sulfuric Acid Etch	5-9	5157** [*]	1670*	40.0*	22.5*
ADHESIVE C with Paste Type Sodium Dichromate Sulfuric Acid Etch for Field Application	2-1/2	5057**	546	5.5	11.0
Adhesive, Adherend, & Surface Treatment					
7075-T6 Bare Aluminum Alloy, Paste Type Sodium Dichromate Sulfuric Acid Etch					
ADHESIVE A	8	2367	1711	2.5	3.1
ADHESIVE B	3	639	2302	1.9	7.9
ADHESIVE C	8	690	2527	2.5	5.5
17-7 PH Stainless Steel, Paste Type Hydrogen Peroxide Etch					
ADHESIVE A	6	2625	1720		
ADHESIVE B	6	1574	2417		
ADHESIVE C	6	465	5172		

* Previously Reported Date
** Failure in Adherends

TABLE 36

EFFECT OF SURFACE ROUGHNESS ON ADHESIVE STRENGTH
AND TOUGHNESS AT VERY LOW TEMPERATURE
(ADHESIVE C)

(7075-T6 Bare Aluminum)

Surface Roughness*	Cure at RT, Days	Tensile Shear, psi		Tee Peel, lbs/1"	
		-320°F	RT.	-320°F	RT
#1. Scribed Diagonal Lines	6	5075**	1026	15.5	21.5
#2. Sandblast	6	5238**	1210	29.0	21.5
#3. Polished Surface	6	5375**	1217	11.5	21.0
#4. Sanded with #36 Garnet Paper	6	5390**	1412	17.5	16.0
#5. Sodium Hydroxide Etched Surface	7-11	5130**	1100	49.5	19.5

* All surfaces were etched with standard sodium dichromate
   sulfuric acid after surface roughening.
** Failure in adherend gripping holes.

The roughened and etched adherends were bonded with Adhesive C at ambient temperature and contact pressure. Tensile shear and tee peel strengths were determined both at -320°F and RT. Results of the study are shown in Table 35. Failure of metallic adherends was experienced with tensile shear at -320°F, eliminating this data from the comparison.

It was concluded that the degree of surface roughness had considerable influence on tee peel strength at the liquid nitrogen temperature. The RT tensile shear and tee peel strengths were not as noticeably affected. No further work was conducted along these lines.

XXI. EVALUATION OF THE DEVELOPED ADHESIVES AGAINST MISCELLANEOUS ADHERENDS

The following alloys are of interest to the National Aeronautics and Space Administration:

Aluminum	Stainless
7075-T6	17-7 PH
2219-T87	301-1/2 Hard
2014-T6	321
6061-T6	
5456-H-343	Titanium
2024-T3 Clad	
	AMS 4910

Adhesive A, B, D and E were selected for evaluating the tensile shear strengt at RT and -320°F when the above adherends were employed. Adhesive C was eliminate from the study because the polymer was common to Adhesive E, which has improved toughness characteristics. Adhesive F was eliminated from the study since the 700°F processing temperature was not compatible with aluminum alloys.

Surface preparation for the aluminum alloys, without exception, was the standar sodium dichromate sulfuric acid etch. Stainless steel preparation was the hydroge peroxide etch. Titanium preparation was a nitric/hydrofluoric acid etch. These surface treatments have been previously described. All alloys were die-punched into the standard breakaway type panels, with the exception of 2219-T87, which was 0.100" thick, and the 301-1/2 hard stainless. The standard 4" x 9" MIL-A-5090D type panel was used for the latter. All joints were one-half overlap cured at room temperature and contact pressure.

Table 37 and Figures 27, 28, 29 and 30 show the results of this study. The 6061-T6 alloy was the most difficult aluminum to bond, the RT and -320°F tensile shear strengths being lower than for all other aluminum alloys. The 301 alloy was the most difficult stainless alloy to bond, again the RT and -320°F tensile shear strengths being lower than for all other stainless alloys.

It was concluded that surface preparation studies would have to be made of each alloy before complete conclusions could be drawn. Tee peel testing was eliminated from this study because of the adherend thickness and individual bend strength variables associated with different alloys.

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TABLE 37

EVALUATION OF THE DEVELOPED ADHESIVES AGAINST MISCELLANEOUS ADHERENDS

Tensile Shear Strength

ALLOYS	ADHESIVE A						ADHESIVE B						ADHESIVE D						ADHESIVE E					
	R.T.			-320°F			R.T.			-320°F			R.T.			-320°F			R.T.			-320°F		
	Cure	GLT	psi	Cure	GLT	psi	Cure	GLT	psi	Cure	GLT	psi	Cure	GLT	psi	Cure	GLT	psi	Cure	GLT	psi	Cure	GLT	psi
ALUMINUM ALLOYS																								
0.063" 7075-T6 Bare Aluminum	7-15	--	3127	7-15	--	2710	8-16	--	1972	8-16	--	5090*	7	--	1960	7	--	5198*	7	--	1073	7	--	5258*
0.100" 2219-T87 Aluminum	8	.002	1892	8	.003	2980	7	.004	1980	7	.003	3470	6	.005	1380	6	.005	4410	6	.011	708	6	.012	7310*
		.004	2110		.004	2830		.004	2130		.005	1720		.005	1556		.005	7220		.012	1052		.013	7190*
		.004	2060		.004	2940		.005	1920		.005	3690		.005	1684		.005	5230		.011	850		.010	6950
		.003	1750		.003	2180		.004	1340		.004	2840		.005	1066		.004	5550		.012	1036		.010	6800
		Avg.	1953		Avg.	2732		Avg.	1842		Avg.	2930		Avg.	1421		Avg.	5602		Avg.	911		Avg.	7062
0.063" 2014-T6 Aluminum	7	.005	1810	8	.004	2750	6	.004	1780	8	.004	4560*	5	.005	1410	7	.004	1840	5	.008	848	7	.011	4800*
		.005	2550		.004	2210		.006	1570		.005	2720		.005	1550		.006	1090		.009	908		.012	4690*
		.005	2230		.007	2310		.007	1998		.008	2250		.006	1440		.007	2320		.010	952		.012	5100*
		.006	2630		.007	2200		.006	2150		.010	1880		.005	1390		.008	2680		.010	984		.013	5150*
		Avg.	2305		Avg.	2367		Avg.	1875		Avg.	2852		Avg.	1447		Avg.	2482		Avg.	923		Avg.	4935
0.063" 6061-T6 Aluminum	7	.006	2320	9	.008	1990	6	.006	1826	8	.007	1100	5	.007	908	7	.007	1460	5	.012	706	7	.014	3580*
		.009	2370		.007	1840		.007	1954		.009	2040		.008	764		.007	1740		.013	824		.016	3650*
		.006	2560		.009	2270		.006	1844		.009	1120		.007	1018		.008	1920		.013	804		.016	3600*
		.009	2250		.010	1150		.010	1680		.010	1290		.012	924		.009	1280		.014	724		.016	3500*
		Avg.	2375		Avg.	1812		Avg.	1826		Avg.	1387		Avg.	903		Avg.	1600		Avg.	764		Avg.	3582
0.063" 5456-H-343 Aluminum	7	.002	2860	9	.005	3180	6	.002	2030	8	.004	3430*	5	.001	1318	7	.003	3300*	5	.006	836	7	.010	3390*
		.006	2480		.004	3420*		.006	1920		.007	2380		.002	1618		.003	3420*		.008	918		.010	3260*
		.006	2610		.008	3160		.010	2240		.006	2240		.007	1070		.004	3430*		.068	922		.011	3630*
		.008	2560		.013	2490		.006	1830		.007	2240		.001	650		.003	3270*		.010	876		.011	3530*
		Avg.	2627		Avg.	3062		Avg.	1995		Avg	2572		Avg.	1089		Avg.	3355		Avg.	888		Avg.	3452
0.063" 2024-T3 Clad Aluminum	7	.005	2300	10	.005	2240	6	.004	3300	9	.004	3300	5	.003	1324	8	.006	3300	5	.010	888	5	.011	3440*
		.008	2626		.008	2210		.005	1386		.003	4100		.004	1732		.008	3200		.009	966		.011	3900*
		.008	2630		.008	2140		.004	1630		.004	3520		.003	1656		.005	3280		.011	954		.010	4250*
		.008	2360		.006	2680		.004	1570		.005	3680		.003	1182		.006	3420		.008	970		.010	4000*
		Avg.	2477		Avg.	2318		Avg.	1499		Avg.	3650		Avg.	1473		Avg.	3300		Avg.	944		Avg.	3898
STAINLESS STEEL ALLOYS																								
0.050" 17-7 PH Stainless** Steel	6	--	2462	6	--	1530	6	--	1843	6	--	1700	NO DATA						NO DATA					
0.063" Type 321 Stainless Steel	6	.001	1750	8	.009	1610	6	.003	1384	8	.010	2790	6	.003	1050	7	.009	3870	5	.008	820	7	.014	6460
		.007	1700		.011	1540		.009	1620		.013	1660		.010	646		.011	4070		.015	780		.016	6220
		.008	1448		.012	1440		.011	1422		.015	1900		.008	878		.013	4390		.015	830		.016	7210
		.009	1450		.010	1230		.012	1410		.012	1960		.009	720		.011	4020		.016	790		.010	6400
		Avg.	1587		Avg.	1455		Avg.	1459		Avg.	2077		Avg.	811		Avg.	4075		Avg.	805		Avg.	6572
0.063" Type 301 1/2 Hard Stainless Steel	8	.007	2080	8	.006	1040	7	.004	644	9	.005	1000	6	.005	930	6	.005	4480	6	.014	594	8	.010	2900
		.009	2740		.007	568		.005	680		.005	1270		.005	580		.005	4620		.013	548		.012	3120
		.009	2060		.006	540		.006	474		.004	1304		.005	384		.005	2480		.014	600		.011	3920
		.007	2760		.005	452		.004	1120		.004	1442		.004	824		.004	2800		.013	616		.010	4720
		Avg.	2410		Avg.	649		Avg.	729		Avg.	1254		Avg.	679			3595		Avg.	589		Avg.	3665
TITANIUM ALLOYS																								
0.050" AMS 4910 Titanium**	6	--	2448	6	--	1325	6	--	1583	6	--	986	NO DATA						NO DATA					

* Failure in gripping ends of metallic adherends

** Previously generated data

Tensile Shear Specimens -- Standard breakaway panels, except as noted. Surface preparations: aluminum, sodium dichromate sulfuric acid etch; stainless steel, hydrogen peroxide etch; and titanium, nitric/hydrofluoric acid etch. Bonded with half-inch overlap at R.T. and contact pressure. NOTE: 2219-T87 Aluminum and 301-1/2 Hard stainless steel were 4" x 9" MIL-A-5090D solid panels with half-inch overlap and sawed to 1" width. Tested per MIL-A-5090D. Average of four specimens.
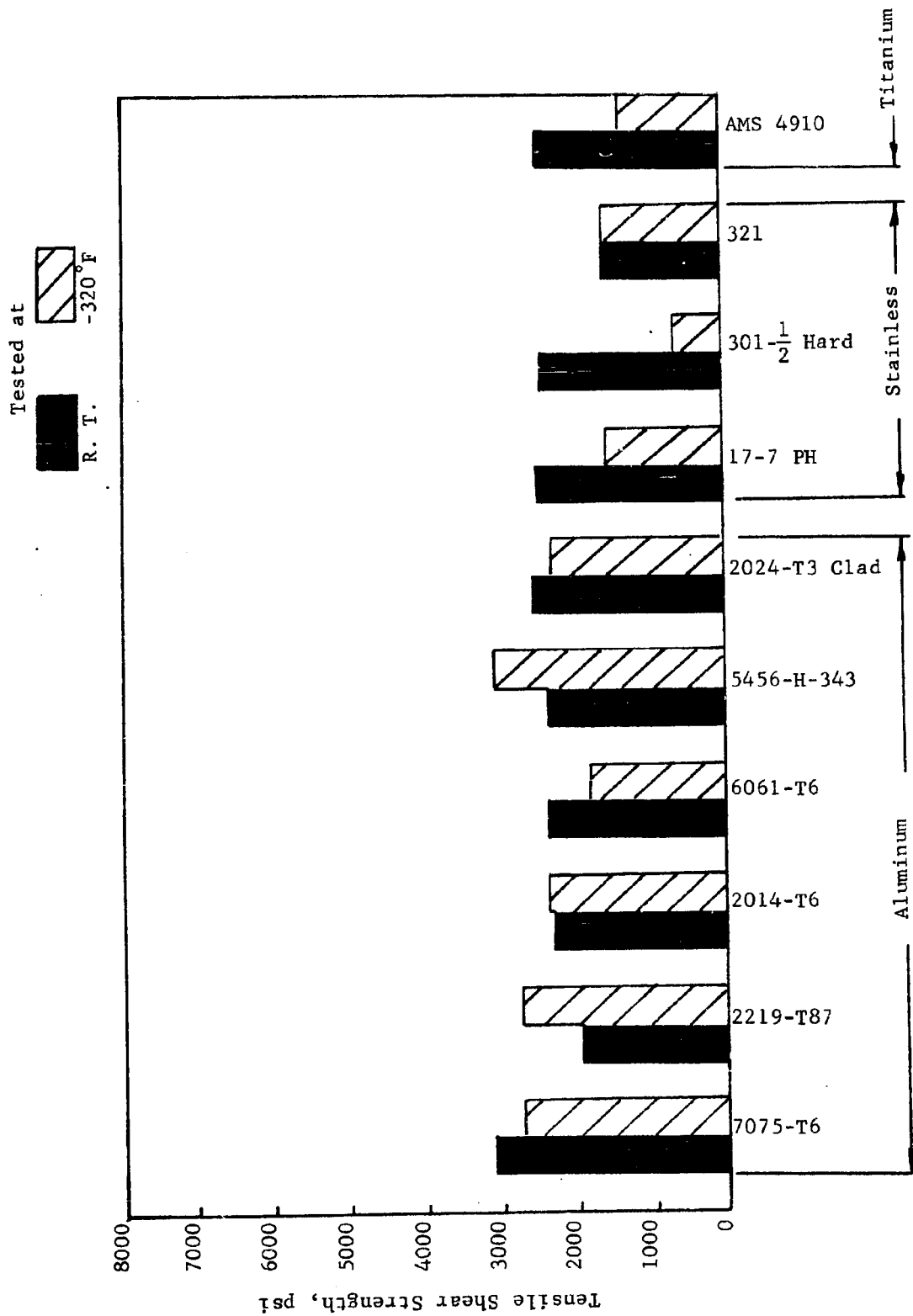
Figure 27. Evaluation of ADHESIVE A against miscellaneous adherends

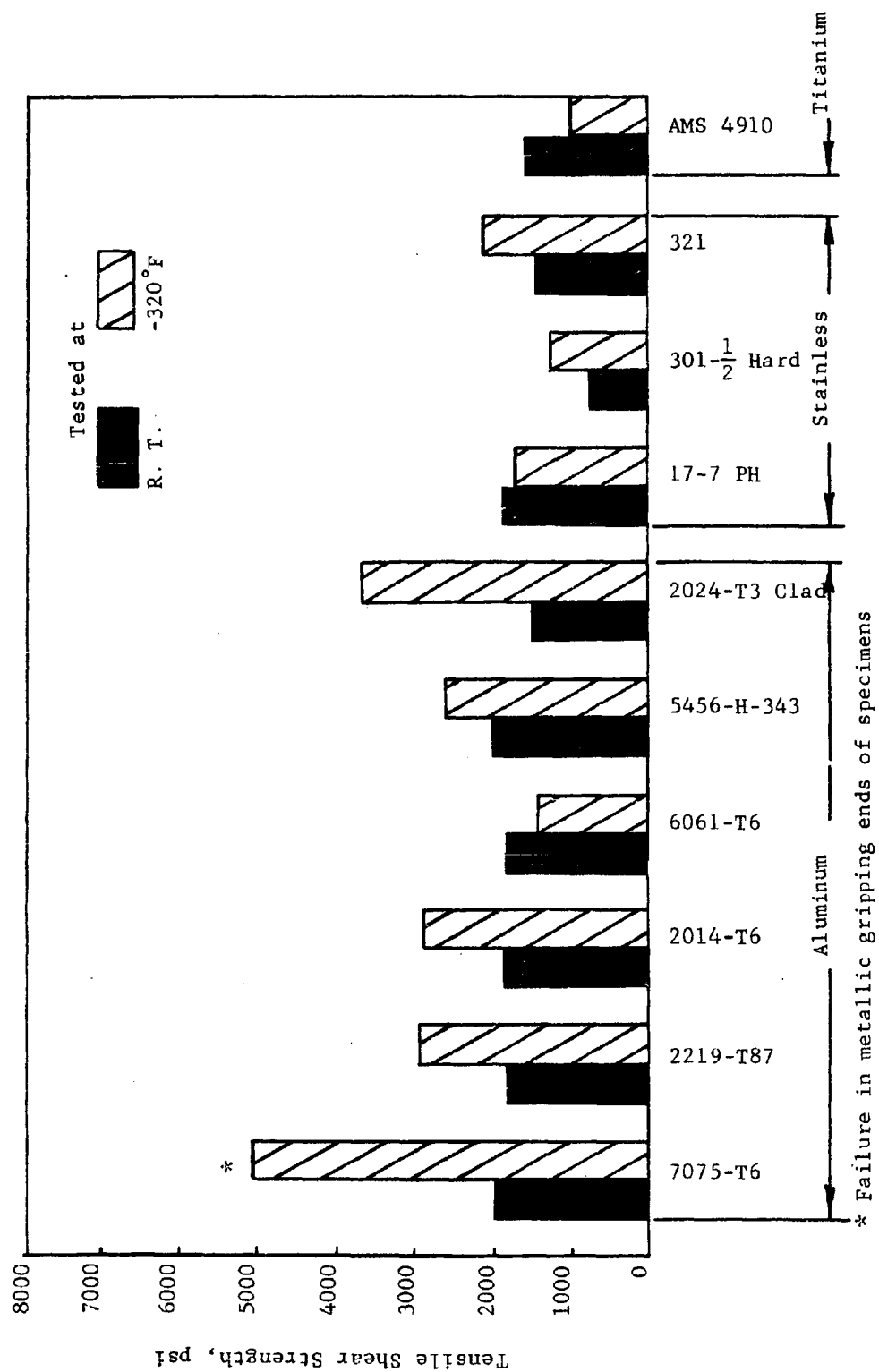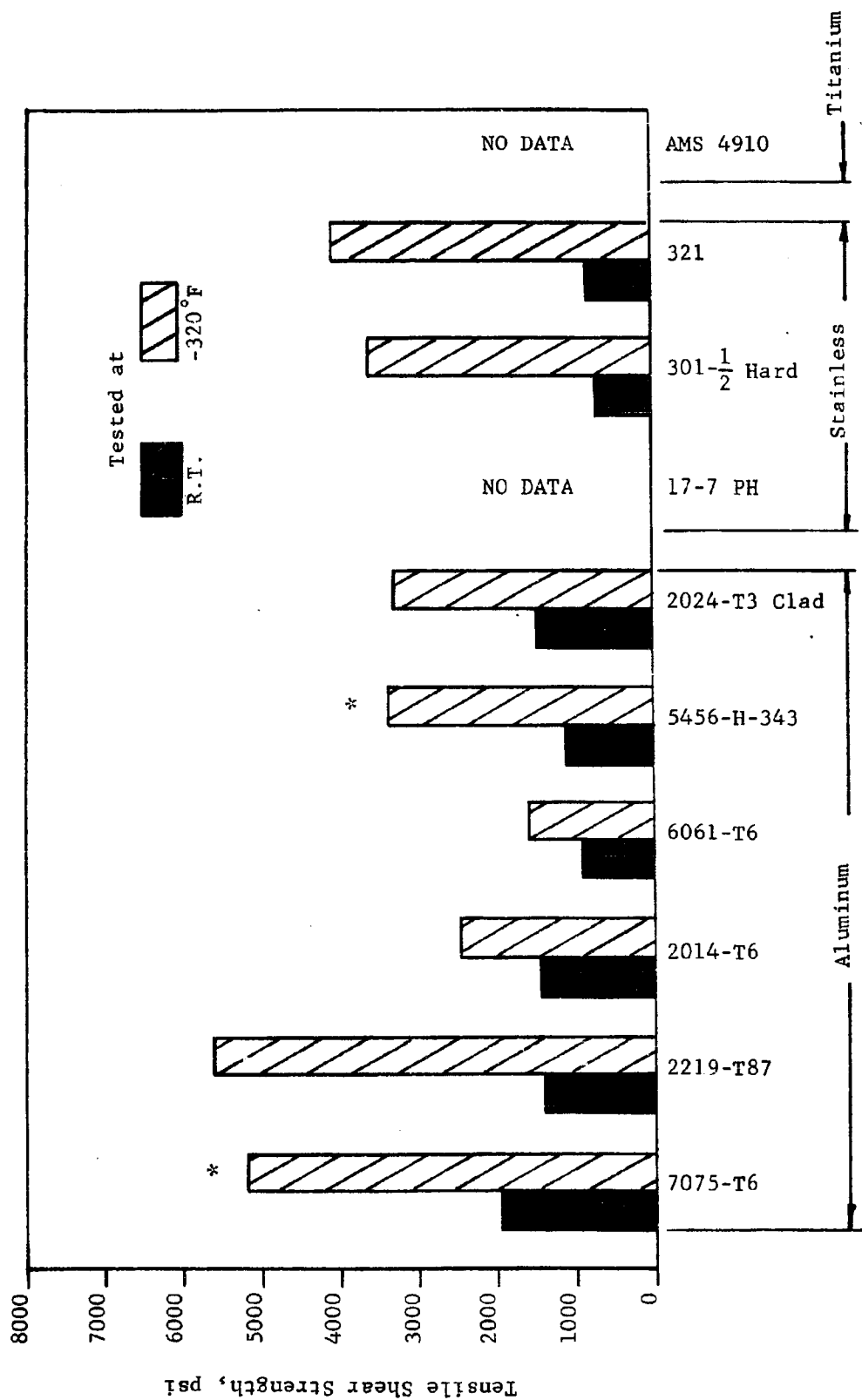Figure 28. Evaluation of ADHESIVE B against miscellaneous adherends

Figure 29. Evaluation of ADHESIVE D against miscellaneous adherends

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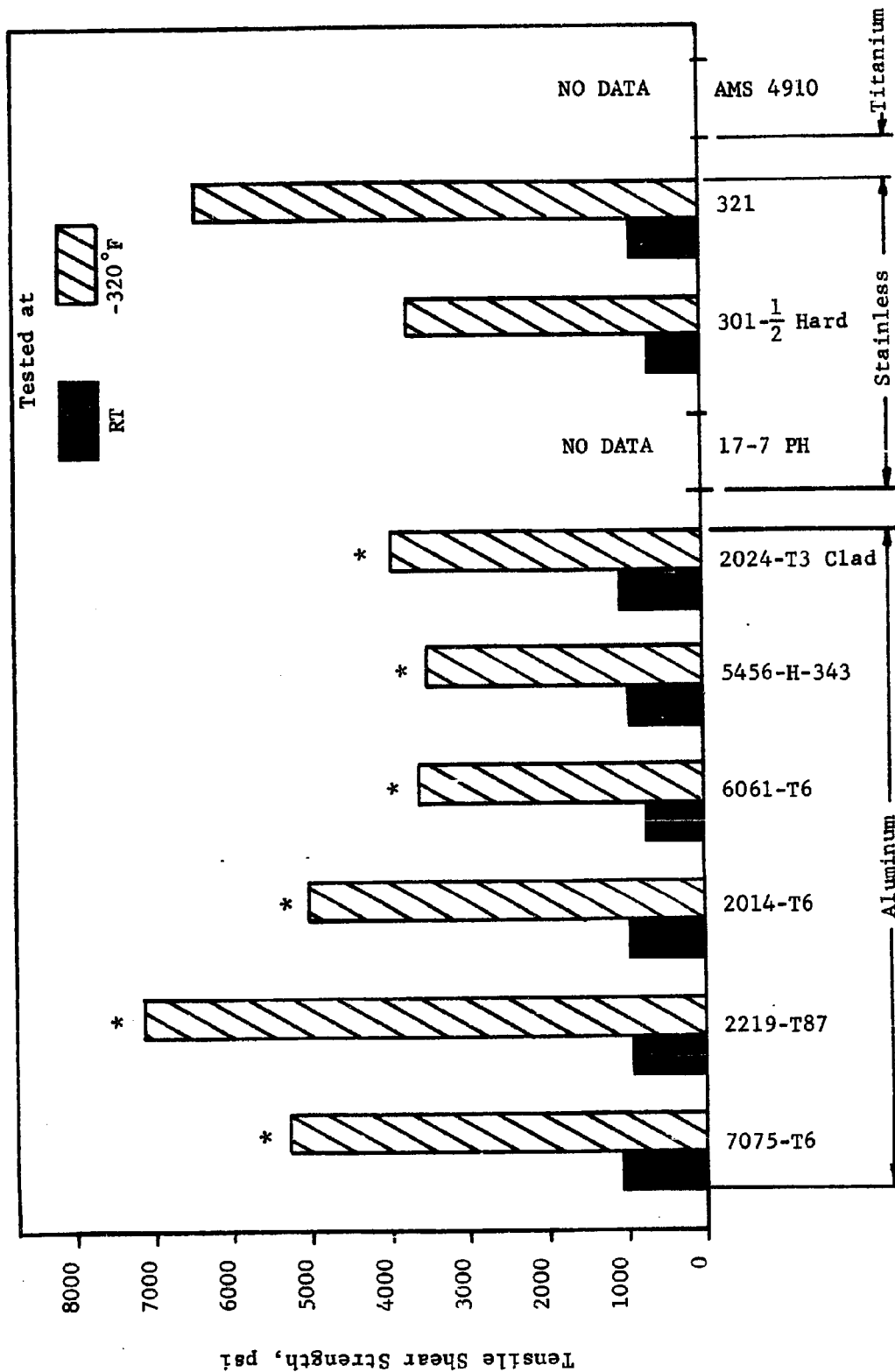
Figure 30. Evaluation of ADHESIVE E against miscellaneous adherends

* Failure in metallic gripping ends of specimens

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In order to supply additional design information regarding the developed adhesive systems, tensile shear strength data were developed at RT and -320°F for Adhesives A, B, and C on stainless (17-7 PH) and titanium (AMS 4910). Table 38 shows these data. Unexpectedly, both Adhesive A and B yielded lower adhesive strength at -320°F than at RT. In general, bond strengths were lower than with 7075-T6 bare aluminum adherends.

XXII. COMPREHENSIVE EVALUATION OF THE DEVELOPED ADHESIVE SYSTEMS AT VERY LOW TEMPERATURE

A. Tensile Shear

Tensile shear strength data were collected for the six developed adhesives (Adhesives A, B, C, D, E, and F) over the temperature range from -423°F to +180°F. The data are shown in Table 39 and schematically in Figure 31. The adherend chosen for evaluation was 7075-T6 bare aluminum alloy with sodium dichromate sulfuric acid etch. Specimens were bonded at room temperature and contact pressur Testing was per MIL-A-5090D.

At the liquid hydrogen temperature, Adhesive C gave the highest test values (8050 psi) and Adhesive A the lowest values. At room temperature, Adhesive A gave the highest test values (3127 psi) and Adhesive E the lowest. At 180°F all tensile shear strength test values were below 1000 psi. All strengths tended to approach zero at 200°F.

B. Tee Peel

Tee peel strength data were collected for the six developed adhesives (Adhesi A, B, C, D, E, and F) over the temperature range from -423°F to +180°F. The data are shown in Table 40 and schematically in Figure 32. The adherend chosen for evaluation was 7075-T6 bare aluminum alloy with a sodium dichromate sulfuric acid etch. Test specimens were bonded at room temperature and contact pressure. Testing was conducted at a head separation of 2"/min.

At the liquid hydrogen temperature, Adhesive E gave the highest test values (44.0 lbs/1") and Adhesive A gave the lowest. At room temperature, Adhesive D gave the highest test values (30.0 lbs/1"). At 200°F the tee peel strengths all tended to approach zero.

C. Mechanical Shock Tests at -423°F

It was felt that the mechanical shock test at liquid hydrogen temperature had been perfected to the point where test conditions were reproducible and where reliable shock data on specimens could be collected.

To minimize the number of specimens required, an arbitrary test procedure was established. Five adhesives were candidates for testing namely Metlbond 406 and Resin 3135/7111, and the developed adhesives A, B, C, D, and E. One set of specimens of each adhesive was first shocked 6 times at 100G level, reporti "GO" if the specimens withstood 6 shocks and "NO GO" if they failed to withstand

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In order to supply additional design information regarding the developed adhesive systems, tensile shear strength data were developed at RT and -320°F for Adhesives A, B, and C on stainless (17-7 PH) and titanium (AMS 4910). Table 38 shows these data. Unexpectedly, both Adhesive A and B yielded lower adhesive strength at -320°F than at RT. In general, bond strengths were lower than with 7075-T6 bare aluminum adherends.

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At the liquid hydrogen temperature, Adhesive E gave the highest test values (44.0 lbs/1") and Adhesive A gave the lowest. At room temperature, Adhesive D gave the highest test values (30.0 lbs/1"). At 200°F the tee peel strengths all tended to approach zero.

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To minimize the number of specimens required, an arbitrary test procedure was established. Five adhesives were candidates for testing namely Metlbond 406 and Resin 3135/7111, and the developed adhesives A, B, C, D, and E. One set of specimens of each adhesive was first shocked 6 times at 100G level, reporting "GO" if the specimens withstood 6 shocks and "NO GO" if they failed to withstand

TABLE 38

EVALUATION OF THE DEVELOPED ADHESIVES
AGAINST MISCELLANEOUS ADHERENDS

Adherend and Surface Preparation	Cure at RT, days	ADHESIVE A		ADHESIVE B		ADHESIVE C	
		-320°F	RT	-320°F	RT	-320°F	RT
1. 17-7 PH Stainless Steel Hydrogen Peroxide Surface Treatment	6	1530	2462	1700	1843	4105	452
2. AMS 4910 Titanium *Conc. HNO3 30 pbw Hydrofluoric 5 pbw Water 100 pbw	6	1325	2448	986	1583	3997	444

Tensile Shear Specimens — .064" 7075-T6 Bare aluminum alloy breakaway panels bonded with 1/2" overlap at ambient temperature and pressure. Tested per MIL-A-5090D. Average of four specimens.

*Guttmann, W. H. "Concise Guide to Structural Adhesives," Method II, p. 23 (Reinhold).

TABLE 39

TENSILE SHEAR STRENGTH EVALUATION OF DEVELOPED ADHESIVES

Adhesive	Cure Time at R.T., days	Tensile Shear Strength, psi					
		-423°F	-320°F	-67°F	R.T.	+125°F	+180°F
ADHESIVE A	7 - 15	2552	2710	3782	3127	1515	544
ADHESIVE B	8 - 16	5352	5090*	3827	1972	1328	738
ADHESIVE C	8 - 18	8050**	5005*	4662	1578	762	454
ADHESIVE D	7	6725*	5198*	5085*	1960	852	353
ADHESIVE E	7	6525	5258*	4542	1073	660	406
ADHESIVE F	15 min. at 700°F	4966	2775	2200	1120	941	801

Specimens: .064" 7075-T6 Bare aluminum alloy breakaway panels with sodium dichromate sulfuric acid etch and bonded at room temperature and contact pressure (except where noted) with 1/2" overlap. Tested per MIL-A-5090D. Average of four specimens.

 * Failure in adherend gripping holes
 ** Doublers used on gripping ends of specimens
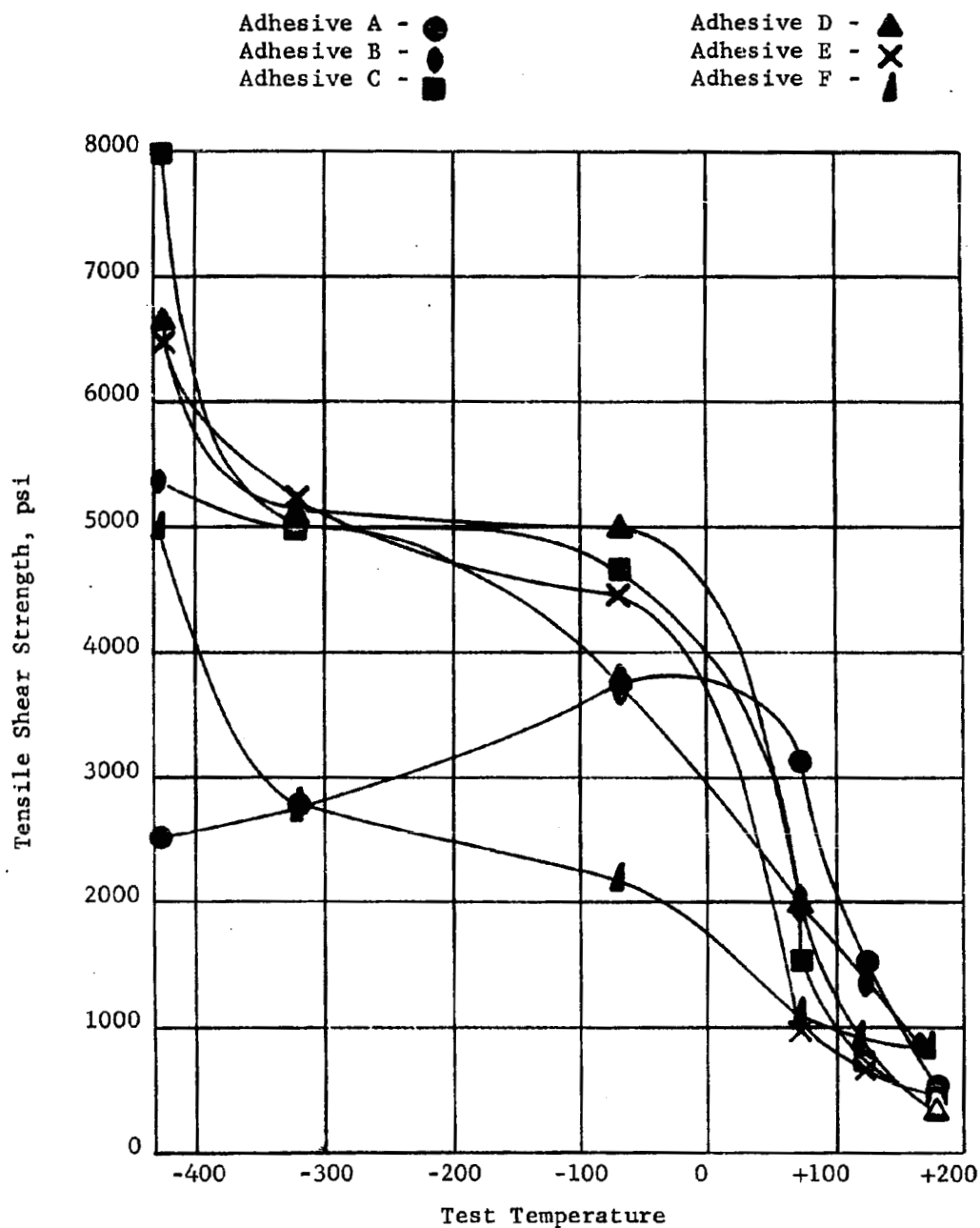
Adhesive A - ●
Adhesive B - ●
Adhesive C - ■

Adhesive D - ▲
Adhesive E - ✕
Adhesive F - ▲

Adherends: .064" 7075-T6 Bare Aluminum
Surface Preparation: Sodium Dichromate Sulfuric Acid Etch
Cure: Room Temperature at Contact Pressure
Testing: MIL-A-5090D

Figure 31. Tensile shear strength evaluation of developed adhesives,

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TABLE 40

TEE PEEL STRENGTH EVALUATION OF
DEVELOPED ADHESIVES

Adhesive	Cure Time at RT,days	Tee Peel Strength, lbs/1"					
		-423°F	-320°F	-67°F	RT	+125°F	+180°F
ADHESIVE A	7-17	3.0	3.5	4.0	3.9	9.0	2.0
ADHESIVE B	8-18	6.3	9.0	7.5	3.6	8.5	2.0
ADHESIVE C	8-18	26.0	33.0	22.5	11.3	9.0	10.0
ADHESIVE D	7-25	26.0	22.5	9.5	30.0	9.0	9.5
ADHESIVE E	7-25	44.0	46.0	14.0	20.0	13.0	11.0
ADHESIVE F	15 minutes at 700°F	38.0	38.0	14.0	4.0	2.5	1.2

Specimens — .020" 7075-T6 Bare aluminum 1" x 12" strips with sodium
dichromate sulfuric acid etch.

Figure 32. Tee peel strength evaluation of developed adhesives.

Adherends: .020" 7075-T6 Bare Aluminum
Surface Preparation: Sodium Dichromate Sulfuric Acid Etch
Cure: Room Temperature at Contact Pressure
Testing: 2"/min Head Travel
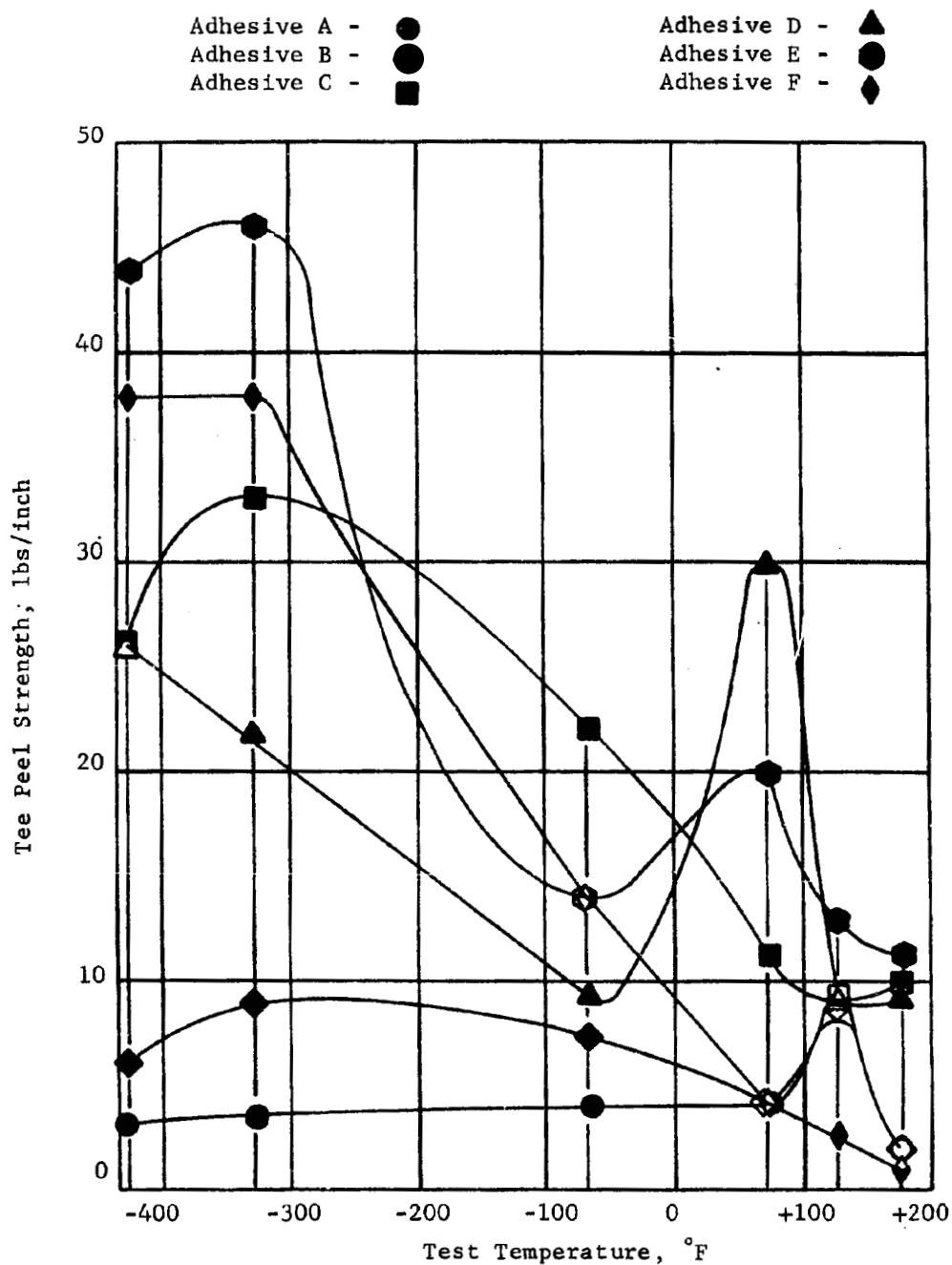
6 shocks. The same procedure was repeated at 50G level. It was anticipated that the adhesives could be subsequently classified according to the G level they were capable of withstanding. See Table 41.

At the 100G level only Adhesive B, C, and D were "GO." At the 50G level Metlbond 406 and Adhesive A and C were "GO." It was expected that Adhesive B would withstand the 100G test and fail the 50G test. The only logical explanation that can be offered is that there tended to be rather erratic scatter in the shock resistance of Adhesive B. This is based on the fact that test conditions were precisely as described. The only solution to this problem would be to test a sufficient number of specimens so that a statistical analysis could be made and an average shock resistance determined. No further testing was conducted in this area.

D. Impact Tests

To supplement the shock data that were collected, it was decided to perform an impact strength test on the existing and newly developed adhesives for purposes of comparison and possible correlation. The test and specimen design employed were identical with that spelled out in Federal Test Method Standard No. 175, Methods 1051 and 1051.1-T. The alloy selected was 7075-T6 bare aluminum. Testing was done at RT and at -320°F. For the -320°F test, the specimens were soaked in liquid nitrogen and transferred to the test fixture within 10 seconds before dropping the pendulum hammer. The rise in temperature by this rapid transfer procedure was determined to be no more than 20°F at the time the specimen was failed.

Table 42 and Figure 33 show the impact strength data that were collected. The newly developed Adhesive A and Adhesive C proved to be the most impact resistant at liquid nitrogen temperature. It was not possible to correlate the RT shock strength with the RT impact strength. Considerable scatter or spread in values was observed in these impact tests, as in shock tests. This discrepancy was believed to be inherent in the specimen design.

E. Butt Tensile Strength

Butt tensile specimens shown in Figure 34 were prepared from 7075-T6 aluminum alloy according to Federal Test Method Standard No. 175, Method 1011.1. Surfaces were prepared for bonding with the standard sodium dichromate sulfuric acid etch and subsequently bonded with Adhesives A, B, and C at ambient temperature and contact pressure. Testing was performed over the temperature range from -423 to +180°F. The data are represented in Table 43 and Figure 35. Stress levels at low temperature were extremely interesting, causing failure in some of the adherends. Stress levels tended to be in the order of 1000 psi at +180°F.

F. Compression Loading of Adhesives

Although no standard test exists for applying compression loads perpendicular to the plane of the glueline of bonded assemblies, the specimen shown in Table 44 was designed. The adherends consisted of 1" x 1" x 3/8" 7075-T6 aluminum alloy blocks bonded on the 1-square-inch sides after preparing the surfaces by sanding. Adhesives A, B, and C were used for bonding at ambient temperature and contact pressure.

TABLE 41

MECHANICAL SHOCK TESTS AT -423°F

Adhesive Systems	Cure Time @ RT, days	G Level	Wave Shape	A Pressure, psi	Number of Shocks	Duration at Chassis, Millisec.	"GO" or "NO GO"
Metlbond 406	*	50	1/2 Sine	30	6	7	GO
Resin 3135/7111	10	50	1/2 Sine	30	1	-	NO GO
ADHESIVE A	14	50	1/2 Sine	30	6	7	GO
ADHESIVE B	30	50	1/2 Sine	30	1	-	NO GO
ADHESIVE C	14	50	1/2 Sine	30	6	7	GO
Metlbond 406	*	100	1/2 Sine	60	1		NO GO
Resin 3135/7111	19	100	1/2 Sine	60	1		NO GO
ADHESIVE A	11	100	1/2 Sine	60	1		NO GO
ADHESIVE B	18	100	1/2 Sine	60	6		GO
ADHESIVE C	14	100	1/2 Sine	60	6		GO
ADHESIVE D	3	100	1/2 Sine	62	6	6	GO
ADHESIVE E	14	100	1/2 Sine	62	6	6	NO GO

Cure: Ambient Temperature and Contact Pressure, except where noted.

*Cured 15 min. at 350°F at 25 psi

TABLE 42

IMPACT STRENGTH EVALUATION OF DEVELOPED ADHESIVES

Adhesive	Cure Time at R.T., days	Impact Strength, ft-lbs/in^2	
		-320°F	R.T.
Resin 3135/7111	3	1.48 2.50 2.86 1.13 1.32 Av. 1.83	14.4 16.6 26.2 Av. 19.0
Metlbond 406	15 min. at 350°F	2.38 3.29 5.67 2.08 2.63 Av. 3.21	11.23 9.1 13.37 7.93 8.7 Av. 10.06
ADHESIVE A	3	8.4 13.8 5.5 16.6 14.0 Av. 10.7	13.3 13.8 14.9 14.5 15.6 Av. 14.4
ADHESIVE B	3	0.94 0.30 0.36 0.50 0.52 Av. 0.65	1.60 2.96 2.50 3.66 2.28 Av. 2.60
ADHESIVE C	3	15.20 5.06 16.40 14.40 14.70 Av. 13.15	14.50 8.80 10.95 13.90 14.70 Av. 12.57

TABLE 42 (Continued)

Adhesive	Cure Time at R.T., days	Impact Strength, ft-lbs/in^2	
		-320°F	R.T.
ADHESIVE D	6	0.62 0.53 1.30 1.47 1.58 Av. 1.10	2.7 2.7 2.85 3.33 3.8 Av. 3.07
ADHESIVE E	5	13.6 13.0 15.1 13.7 15.1 Av. 14.1	2.8 3.7 2.7 3.08 2.8 Av. 3.07

Specimen and Test: Fed. Test Method Std. No. 175, Method 1051

Surface Preparation: Sanding

Cure: Room Temperature and contact pressure

Adherends: 7075-T6 Bare Aluminum
Surface Preparation: Sanding
Cure: Room Temperature at Contact Pressure
Specimen & Test: Fed. Test Method Std. No. 175,
Methods 1051 & 1051.1-T
Pendulum Velocity: 11.0 ft/sec
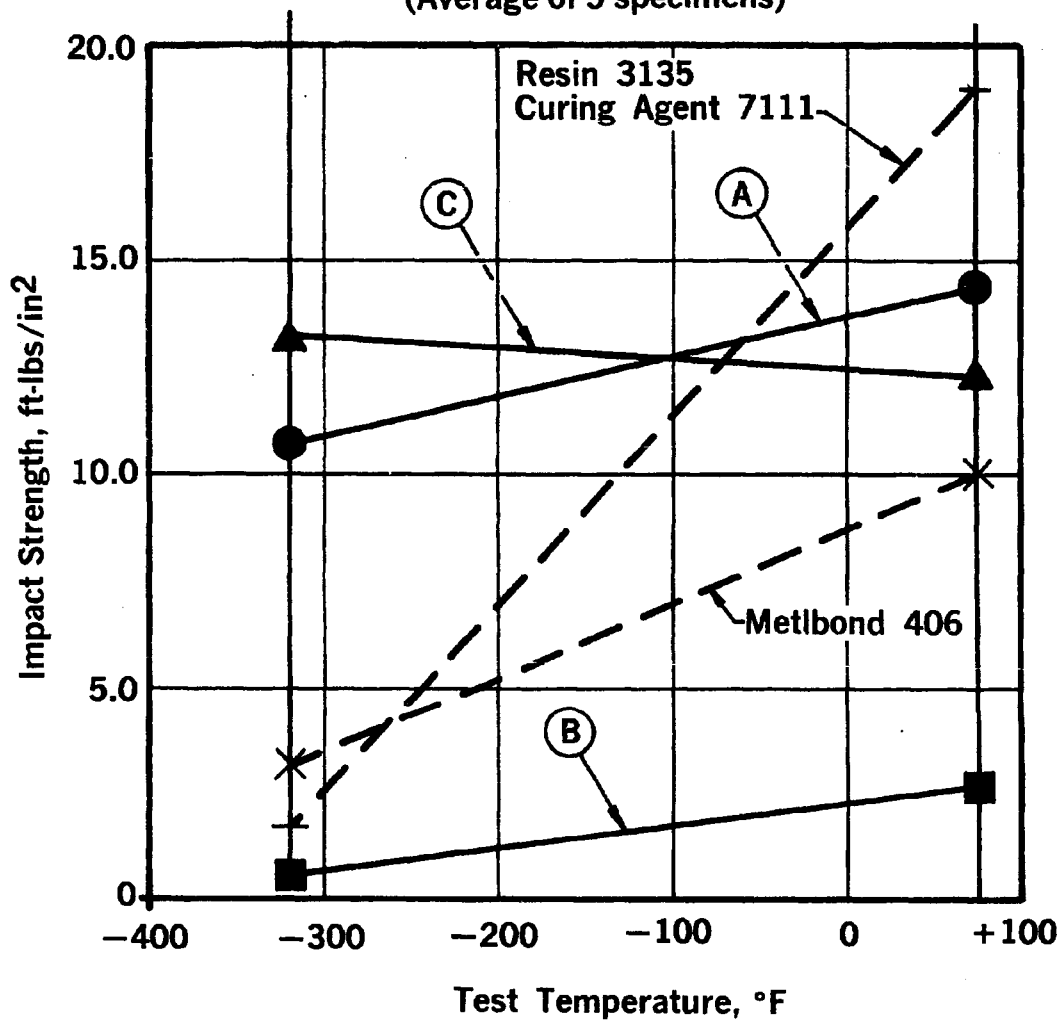**(Average of 5 specimens)**

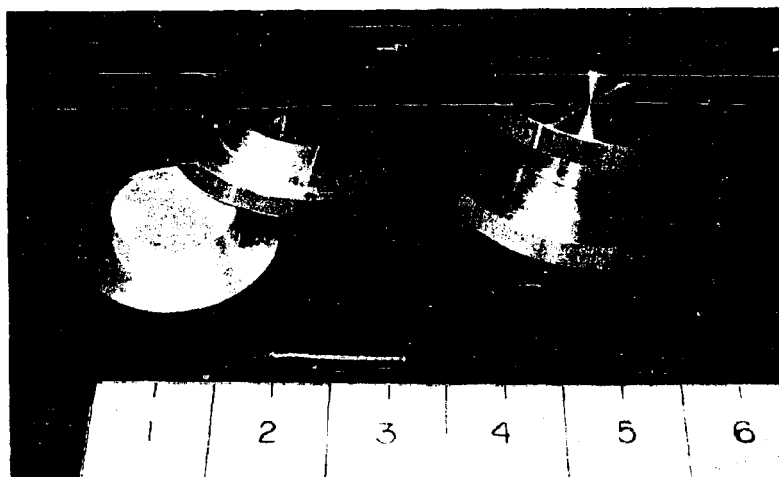Figure 33.   Impact strength evaluation of
newly developed adhesives.

Figure 34. Butt tensile strength specimen
design per Federal Test Method
Standard No. 175, Method 1011.1.

TABLE 43

BUTT TENSILE STRENGTH EVALUATION OF DEVELOPED ADHESIVES

Adhesive	Cure Time at R.T., days	Butt Tensile Strength, psi					
		-423°F	-320°F	-67°F	R.T.	+125°F	+180°F
ADHESIVE A	8 - 9	5700	5470	3930	3200	1250	774
ADHESIVE B	8 - 16	9200*	6100	3180	1900	1655	1000
ADHESIVE C	7 - 15	7600*	6240*	5800	1860	1000	610
ADHESIVE D	9 - 10	6800*	7700*	6360	1910	820	749
ADHESIVE E	3 - 7	6200	5930	4150	795	585	470

Specimen and Test: Fed. Test Method Std. No. 175, Method 1011.1

Surface Preparation: Sodium dichromate sulfuric acid etch.

Cure: Room Temperature and contact pressure.

Adherends: 7075-T6 Bare Aluminum
Surface Preparation: Sodium Dichromate
Sulfuric Acid Etch

Cure: Room Temperature at Contact Pressure
Specimen & Test: Fed. Test Method Std. No. 175,
Method 1011.1
(Single Specimens)
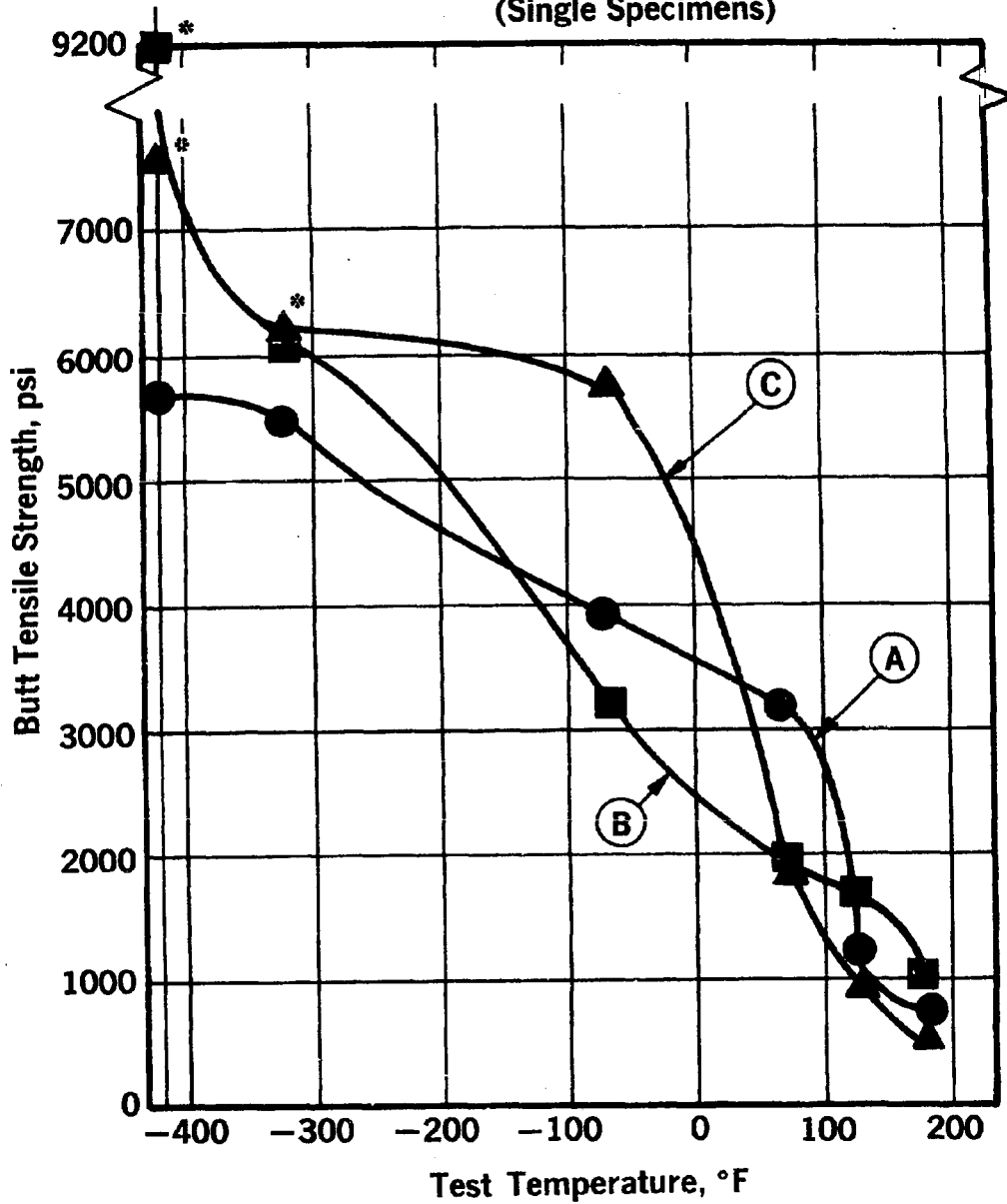
*Failure in Adherends

Figure 35. Butt tensile strength evaluation
of newly developed adhesives.

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TABLE 44

EFFECT OF COMPRESSION LOADS PERPENDICUIAR TO
ADHESIVE GLUELINES AT AMBIENT AND VERY LOW TEMPERATURE

(1" x 1" x 3/8" 7075-T6 Bare Aluminum Alloy with Sodium
Dichromate Sulfuric Acid Etch Bonded 8 Days at Ambient
Temperature at Contact Pressure)
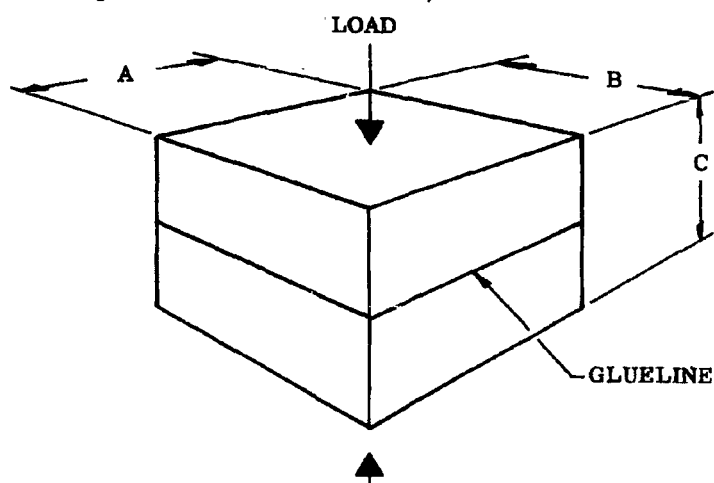
Adhesive System	Test Condition	COMPRESSION LOADING (Dimensions of Specimens in inches)							
		Before Loading			After 20,000 lbs Load	After 40,000 lbs Load	After 60,000 lbs Load		
		A	B	C			A	B	C
ADHESIVE A	RT	1.001	0.999	0.740	No Change	No Change	1.002	1.001	0.741
"	-320°F	1.003	0.997	0.743	"	"	1.003	0.998	0.743
ADHESIVE B	RT	1.001	0.996	0.744	"	"	1.0015	0.997	0.7435
"	-320°F	1.004	0.9965	0.7435	"	"	1.006	0.9977	0.742
ADHESIVE C	RT	1.001	0.995	0.741	"	"	1.002	0.9985	0.7405
"	-320°F	1.001	0.999	0.7416	"	"	1.0035	0.9994	0.740

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Each specimen was measured carefully in its three major planes prior to testing. A compression load of 20,000 pounds was applied over the 1-square-inch surface area. The specimen was then removed and its dimensions again measured. This was repeated after 40,000 and 60,000 pounds compression loading. Testing was performed at RT and also at $-320°F$. No bond failure was experienced, nor were there any dimensional changes noted in the three major planes of the specimens for all three adhesives. It was concluded that there was no compression sensitivity in the adhesives at the temperatures tested. The data are also shown in Table 44.

G. Cure Time Dependence

It was desired to know how the cure time at ambient temperature and contact pressure affected strengths of the developed adhesives. Tensile shear strength at $-320°F$ and RT was chosen as the criteria. Standard half-inch overlap breakaway panels of .064" 7075-T6 bare aluminum alloy with a sodium dichromate sulfuric acid etch were bonded and then tested after 22 hours, 2 days, 3 days, and 4 days at ambient temperature cure.

Table 45 and Figures 36, 37 and 38 show the results of this study. Adhesive A produced an optimum low temperature strength after 22 hours cure; the ambient temperature strength was not optimized until 3-days cure at RT. Adhesive B produced optimum ambient temperature strength after 22 hours; the low temperature strength was equivalent to the ambient temperature strength after 22 hours, but reached an optimum after 3-days cure time. Adhesive C was the slower curing of the developed adhesives; the optimum ambient and low temperature strength was attained after 3-days cure time. Adhesive D produced optimum strength in 2-days cure time at RT. Adhesive E was comparable to Adhesive C. Of these adhesives, Adhesive B exhibited the best balance between low and ambient temperature strength after 22-hours cure.

H. Effect of Temperature Cycling on Adhesive Strength

It was desired to know what affect cycling between liquid nitrogen and ambient temperature would have on the strength of Adhesive A, B, and C bonds. Tensile shear strength at RT was chosen as the criteria. Standard half-inch overlap breakaway panels of .064" 7075-T6 bare aluminum alloy with a sodium dichromate sulfuric acid etch were bonded with each of the three adhesives by curing 8 days at ambient temperature and contact pressure. Subsequently, the bonds were cycled 20 times between $-320°F$ and RT and then tested for RT tensile shear strength. Table 46 shows the results of this study. No loss in strength was noted for any of the adhesives after temperature cycling.

I. Effect of Postcure on RT-Cured Adhesives

It was also desired to know what affect an elevated temperature postcure would have on the strength and toughness of Adhesive A, B, and C bonds after an ambient temperature cure at contact pressure. Half-inch overlap breakaway panels of .064" 7075-T6 bare aluminum alloy and tee peel specimens of .020" 7075-T6 bare aluminum alloy, with a sodium dichromate sulfuric acid etch, were prepared with each adhesive. Control specimens were cured 8 days at ambient temperature prior to testing at $-320°F$

TABLE 45

AMBIENT CURE TIME DEPENDENCE EVALUATION
FOR DEVELOPED ADHESIVES

Adhesive	Cure Time at R.T., days	Tensile Shear Strength, psi	
		-320°F	R.T.
ADHESIVE A	22 Hours	1281	3732
	2 Days	2042	3670
	3	2347	3800
	4	2357	3720
ADHESIVE B	5 Hours	568	284
	8	1088	876
	16	2920	1770
	22	2816	2665
	2 Days	3375*	2520
	3	4900*	2557
	4	3990	2570
ADHESIVE C	22 Hours	1614	306
	2 Days	4072	1416
	3	4837*	1690
	4	5262*	1516
ADHESIVE D	1	2485	1899
	2	5150*	2100
	3	4865*	2102
	4	5125*	1663
ADHESIVE E	1	4250	496
	2	5065*	812
	3	5280*	954
	4	5265*	1048

Tensile Shear Specimens - .064" 7075-T6 Bare aluminum alloy
breakaway panels with sodium di-
chromate sulfuric acid etch and
bonded at room temperature and con-
tact pressure with 1/2" overlap.
Tested per MIL-A-5090D. Average
of four specimens.

* Failue in adherend gripping holes.

Figure 36. Ambient cure time dependence of Adhesive A
on RT and -320°F tensile shear strength.

(.064" 7075-T6 Bare Aluminum Alloy Breakaway Panels
with 1/2" Overlap and Sodium Dichromate Sulfuric
Acid Etch)

* Failure in Adherend Grip Holes
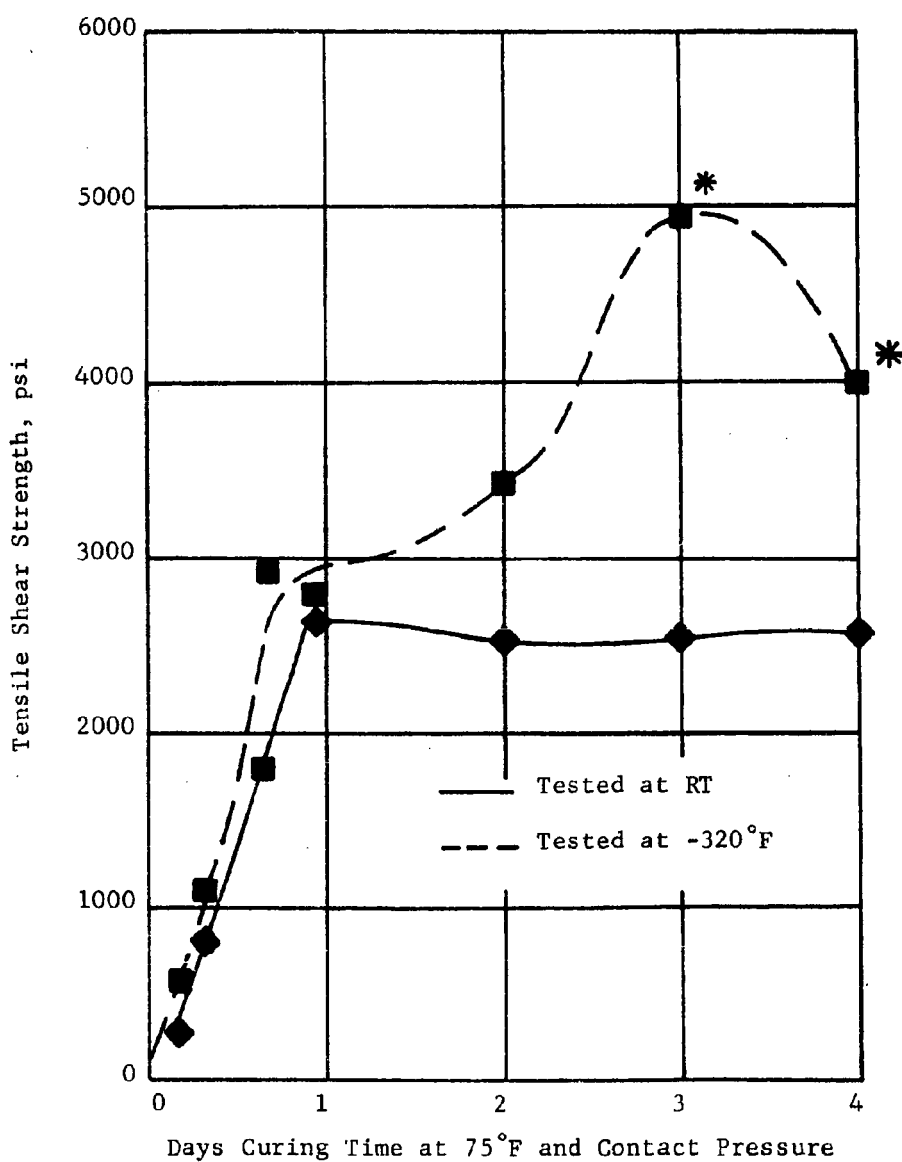
Figure 37. Ambient cure time dependence of Adhesive B
on RT and -320°F tensile shear strength.

Figure 38. Ambient cure time dependence of Adhesive C on RT and -320°F tensile shear strength.

TABLE 46

EFFECT OF TEMPERATURE CYCLING ON THE
BOND STRENGTHS OF LOW TEMPERATURE ADHESIVES
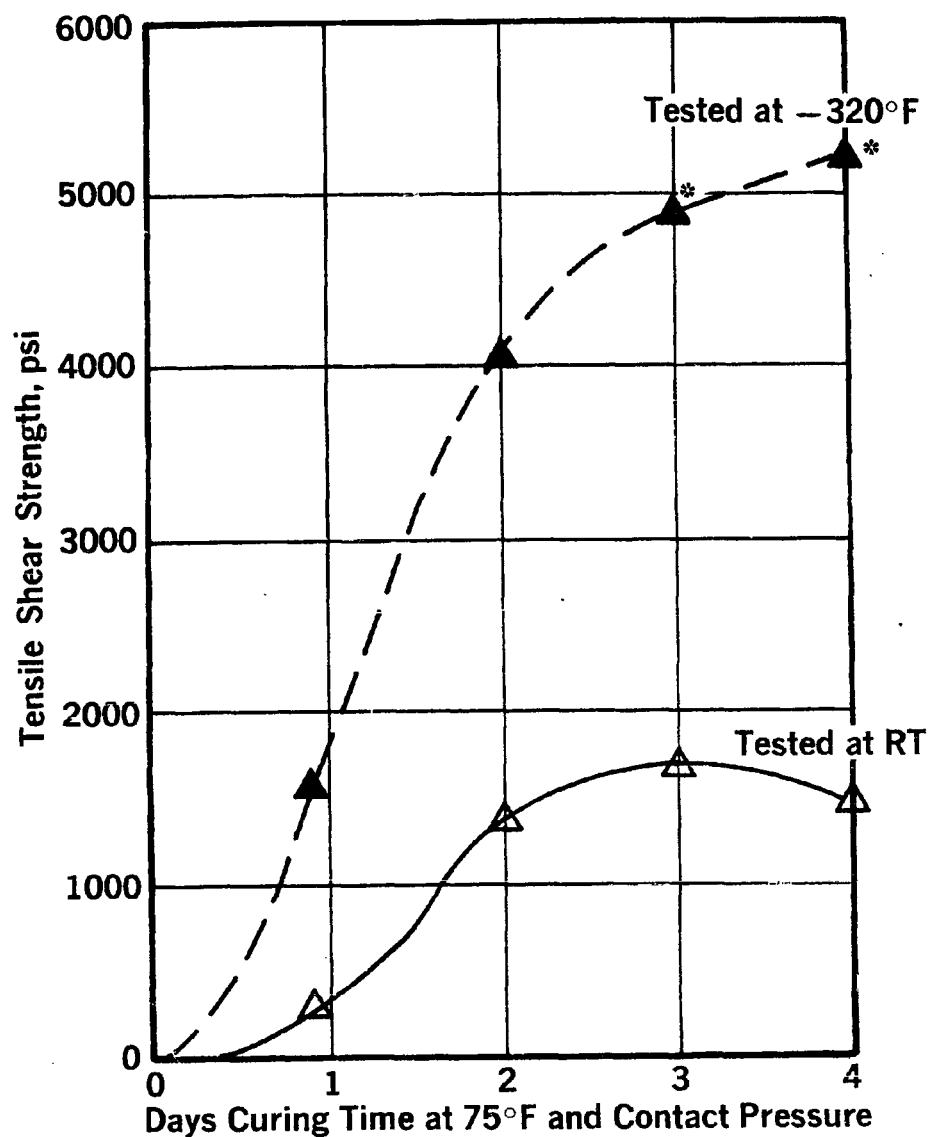
(.064" 7075-T6 Bare Aluminum Alloy
with 1/2" Overlap, Sodium Dichromate
Sulfuric Acid Etch)

| Adhesive System | Cure at RT | RT Tensile Shear Strength, psi* | |
		CONTROL (No Cycling)	CYCLED 20 TIMES from Ambient to -320°F
ADHESIVE A	8 Days	3397	3377
ADHESIVE B	"	2395	2197
ADHESIVE C	"	1805	1867

* Cured 8 days at ambient temperature. Average of 4 specimens

Adherends: .064" 7075-T6 bare aluminum alloy breakaway
panels with 1/2" overlap

Surface Preparation: Sodium dichromate sulfuric acid etch

Testing: Per MIL-A-5090D. Average of 4 specimens

and RT. The remaining specimens were cured 2 days at ambient temperature, followed by a postcure of 1 hour at 200°F prior to testing at the same conditions.

Table 47 shows the results of this study. Postcure tended to significantly upgrade the -320°F and RT tensile shear strength of Adhesives A and B; shear strength of Adhesive C was not noticeably affected. Postcure noticeably improved the -320°F tee peel strength for all adhesives; the RT strength was not appreciably changed.

J. Effect of Glueline Thickness on Epoxy-Polyamide Adhesive Strength

The effect of glueline thickness on adhesive strength is known to be critical. Because an epoxy-polyamide adhesive was common to Adhesives A and B, a study was made of the Resin 3135 and Curing Agent 7111 system. Standard half-inch overlap bonds using .064" 7075-T6 bare aluminum alloy with sodium dichromate sulfuric acid etch were prepared, utilizing various diameter shim wires to attain glueline thickness ranging from 4 to 12 mils. Bonds were cured 10 days at ambient temperature and contact pressure prior to testing in tensile shear at -320°F and RT.

Figure 39 shows the results of this study. It was observed that there was a gradual reduction in -320°F and RT shear strength as the glueline thickness increased from 4 to 12 mils.

K. Effect of Mismatch on Epoxy-Polyamide Adhesive Strength

In many bonding operations it is not always possible to be assured of perfectly planed surfaces or perfectly aligned surfaces for bonding. A study of mismatch was accordingly indicated. Again, an epoxy-polyamide adhesive was chosen for study because this system is common to both Adhesives A and B. Figure 40 shows the specimen design. Two .064" x 1" x approx. 8 3/4" strips of 7075-T6 bare aluminum alloy with sodium dichromate sulfuric acid etch were bonded together. Shims ranging in thickness from approximately 4 to 55 mils were used under one-half of the bonded area, and the other half of the bonded area was accomplished by drawing the .064" adherends tightly together. The shim caused a mismatch depending on its thickness. Immediately adjacent to the shim the adherends were machined for a half-inch overlap shear specimen. Glueline thicknesses in the mismatch ranged from 4 to 55 mils (approximately). RT tensile shear strength was determined for specimens cured 8 days at ambient temperature and contact pressure.

As shown in Figure 40, the RT shear strength tended to increase from a mismatch of 4 mils (3000 psi) to an optimum at 16 mils (4000 psi), then rapidly fell off to a constant level (2000 psi) from about 33 to 55 mils mismatch. Although it was not expected that a mismatch of 16 mils would yield such a high stress level, it was apparent that a minimum stress level of 2000 psi could be expected up to almost 60 mils mismatch.

TABLE 47

EFFECT OF 200°F POSTCURE
ON THE STRENGTH OF THE DEVELOPED ADHESIVES

Adhesive	Cure at RT	Postcure	Tensile Shear Strength, psi		Tee Peel Strength, lbs/1"	
			RT	-320°F	RT	-320°F
Adhesive A	8 Days	None	3555	2400	3.5	3.5
	2 Days	1 Hr. @ 200°F	3920	3172	4.0	4.0
Adhesive B	8 Days	None	2295	2955	4.0	12.0
	2 Days	1 Hr. @ 200°F	2705	4402	2.0	25.0
Adhesive C	8 Days	None	1635	5060*	18.0	55.0*
	2 Days	1 Hr. @ 200°F	1611	4870*	19.0	70.0*

* Failure in Adherends.

Adherends: Tee Peel   - .020" 7075-T6 bare aluminum alloy 1" x 12"
specimens bonded with total overlap
Tensile Shear - .064" 7075-T6 bare aluminum alloy
breakaway panels bonded with 1/2" overlap
Surface Preparation: Sodium Dichromate Sulfuric Acid Etch
Testing: Tee Peel 2"/min head travel
Tensile Shear per MIL-A-5090D
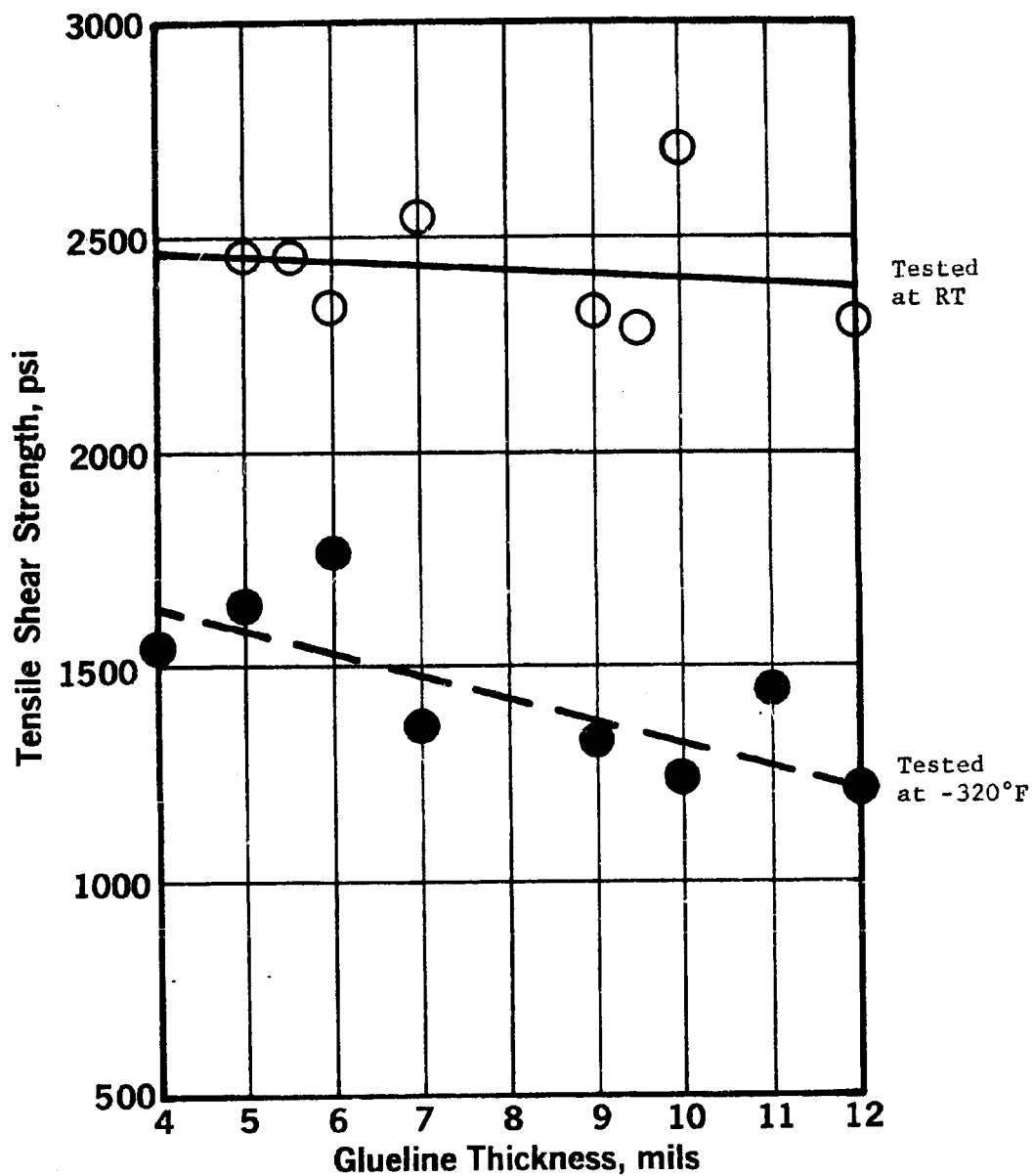
163

(.064" 7075-T6 Bare Aluminum Alloy with
½" Overlap, Sodium Dichromate Sulfuric
Acid Etch)

Figure 39. Typical effect of glueline thickness
on the strengths of an epoxy polyamide*
adhesive system.

* Resin 3135 and Curing Agent 7111.
  Cured 10 days at ambient temperature.
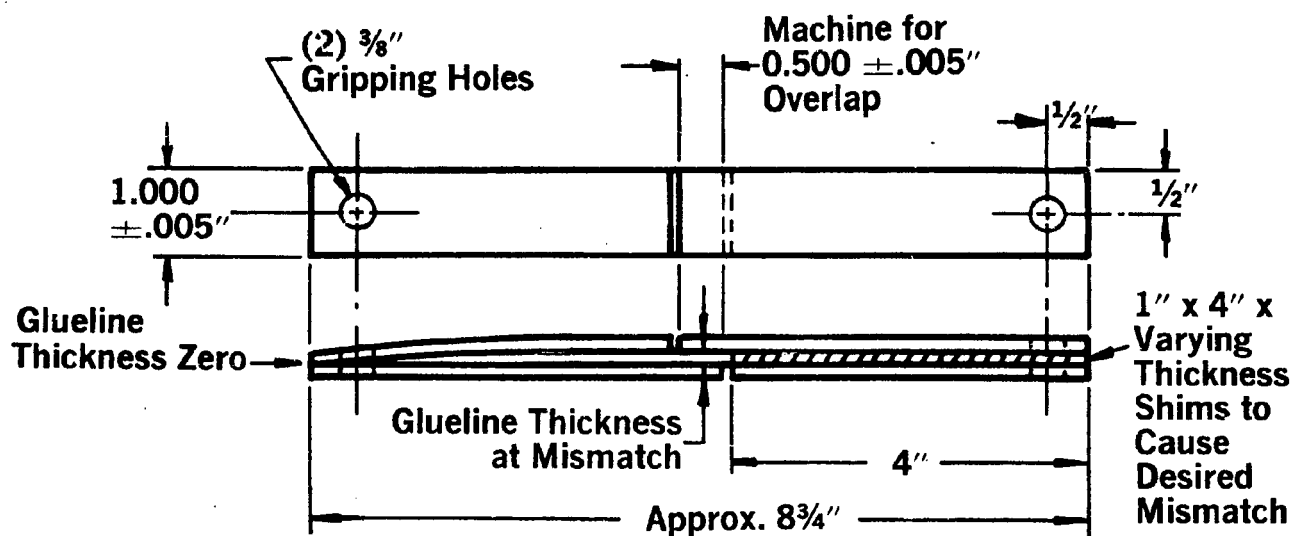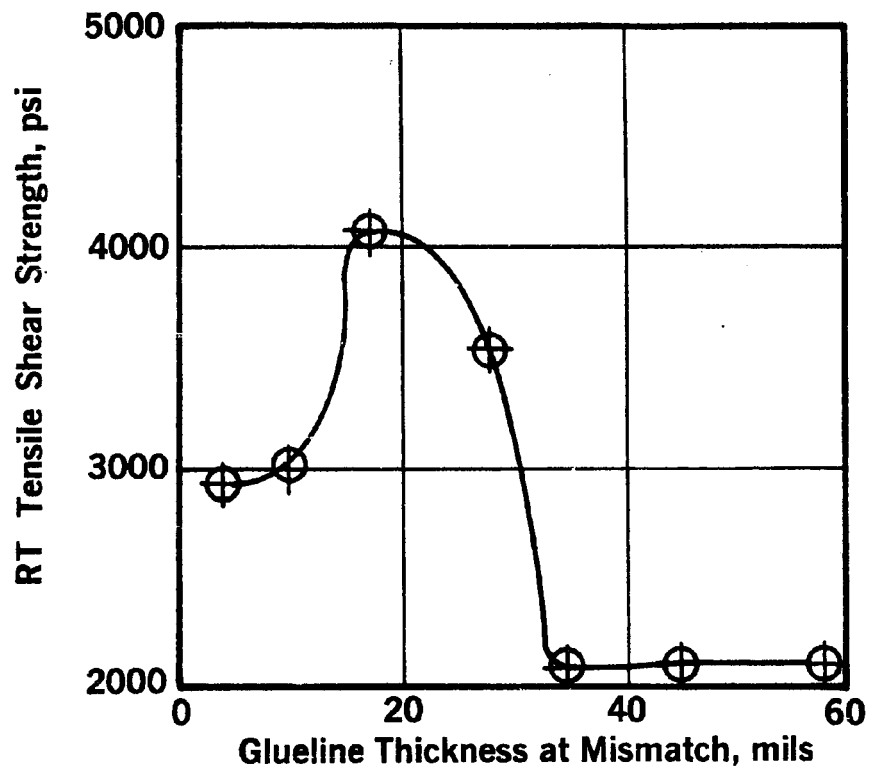
Figure 40. Typical effect of mismatch on the RT strength of an epoxy polyamide* adhesive system.

*Resin 3135 and Curing Agent 7111.
Cured 8 days at ambient temperature.

L. Vibration

The original terms of this work required evaluating adhesives at the liquid hydrogen temperature in vibration, wherein the frequency, G loadings, and displacements were to be varied.

The specimen selected was a half-inch overlap bonded tensile design, machined from 1" x 3/8" 7075-T6 bare aluminum bar stock. Width of the overlap area was necked-down to 0.500". It was intended that the specimen would be loaded as required in tension, and that vibration would be effected by mechanical attachment to the bonded area.

NASA agreed to perform the actual tests. Forty bonded specimens each of Adhesives A, B, and C were submitted for testing. After a great deal of effort had been applied to the test, it was finally concluded that the data collected were not consistent and conclusive. Further vibration testing was abandoned.

MATERIALS IDENTIFICATION

Aclar -- Allied Chemical Corp., General Chemical Division
Aclar 22C -- Allied Chemical Corp., General Chemical Division
Adhesive A -- Narmco Research & Development, a Division of Telecomputing Corporation
Adhesive B -- Narmco Research & Development, a Division of Telecomputing Corporation
Adhesive C -- Narmco Research & Development, a Division of Telecomputing Corporation
Adhesive D -- Narmco Research & Development, a Division of Telecomputing Corporation
Adhesive E -- Narmco Research & Development, a Division of Telecomputing Corporation
Adiprene C -- E. I. duPont deNemours & Company Inc.
Adiprene L-100 -- E. I. duPont deNemours & Company Inc.
Adiprene LD-167 -- E. I. duPont deNemours & Company Inc.
Adiprene LD-213 -- E. I. duPont deNemours & Company Inc.
AF-40 -- Minnesota Mining & Manufacturing Co.
AF-41 -- Minnesota Mining & Manufacturing Co.
Alodine treatment -- Anadite Inc., 10630 Sessler St., South Gate, Calif.
Anodize treatment -- Anadite Inc., 10630 Sessler St., South Gate, Calif.
APCO-1261 -- Applied Plastics Division, Hexcel Products Company
BCI-819 -- Belding Corticelli Industries, Inc.
BCI-1107 (nylon type 11) -- Belding Corticelli Industries, Inc.
BCI-3218 (alkylated nylon, type 8) -- Belding Corticelli Industries, Inc.
Bondaid -- W. S. Shamban & Company
BRL-2741 -- Bakelite
CSC #3801 -- Chem Seal Corporation of America
Curing Agent D -- Shell Chemical Company
Curing Agent U -- Shell Chemical Company
Curing Agent 7111 -- Narmco Materials Division, Telecomputing Corporation
Curing Agent 7125 -- Narmco Materials Division, Telecomputing Corporation
Curing Agent 7133 -- Narmco Materials Division, Telecomputing Corporation
Curing Agent 7139 -- Narmco Materials Division, Telecomputing Corporation
DBVIII -- Argus Chemical
DC A-4014 -- Dow Corning Corporation
DC RTV 11 -- Dow Corning Corporation
DC Q-2-0103-2 -- Dow Corning Corporation
Delrin -- DuPont
DEN-438 -- Dow Chemical Company
DER-331 -- Dow Chemical Company
DER-332 -- Dow Chemical Company
DMF (dimethylformamide) -- DuPont
DSA (dodecenylsuccinic anhydride)
Eastman 910 -- Eastman Kodak Company
EC-1933B/A -- Minnesota Mining & Manufacturing Co.
Elvanol -- DuPont
Empol 1014 -- Emery Industries
Empol 1024 -- Emery Industries

Epi-Cure 855 -- Jones-Dabney
Epi-Rez 510 -- Jones-Dabney
Epi-Rez 5042 -- Jones-Dabney
Epi-Rez 5132 -- Jones-Dabney
Epi-Rez 5163 -- Jones-Dabney
Epon 812 -- Shell Chemical Company
Epon 828 -- Shell Chemical Company
ERL 0625 -- Union Carbide Plastics Co.
Estane 5740x1 -- B. F. Goodrich Chemical Co.
Estane 5740x2 -- B. F. Goodrich Chemical Co.
FM-63 nylon -- Plastex Process Co., Maywood, N. J.
FM-1000 -- Bloomingdale Rubber Co.
GE RTV-40 -- General Electric Co.
GE RTV-60 -- General Electric Co.
GE XS-4004 -- General Electric Co.
Genamid 2000 & 250 -- General Mills Chemical
Hetron 32A -- Durez Plastics Div., Hooker Chemical Corp.
Hetron 92 -- Durez Plastics Div., Hooker Chemical Corp.
HG-32 Glass Skrim Cloth -- Hess Goldsmith
HHPA (hexahydrophthalic anhydride)
HMDI (hexamethylene diisocyanate)
Hypalon 40 -- DuPont
Kel-F -- R. S. Hughes Co., Inc., 4515 Alger St. Los Angeles 39, Calif.
Kel-F film, etches -- W. S. Shamban & Company
Kel-81 & 82 -- Minnesota Mining & Manufacturing Co.
Kynar -- Pennsalt Chemicals
Lancast A -- Ciba Company
Lexan -- General Electric
LHT-240 -- Union Carbide Chemicals Company
LM-52 -- Union Carbide Chemicals Company
Lucite 204-X -- DuPont
MD-551 -- Enjay Company, Inc.
MDA (methylene dianiline) -- Matheson Coleman & Bell
Metlbond 406 -- Narmco Materials Division, Telecomputing Corporation
Metlbond 408 -- Narmco Materials Division, Telecomputing Corporation
Metlbond 409 -- Narmco Materials Division, Telecomputing Corporation
MNA (methyl nadic anhydride)
Moca -- E. I. duPont deNemours & Company
Mondur CB75 -- Mobay Chemical Company
Multranil 176 -- Mobay Chemical Company
Multron R12 -- Mobay Chemical Company
Mylar -- DuPont
Nylon Marquisette -- Burlington Industrial Fabrics Company
Nylon 7 -- Union Carbide Chemicals Company
Ny-Sul-Loft 1370 -- Burlington Industrial Fabrics Company

Parlon 300 -- Hercules Powder Company
Pentamide 1 -- Heyden Newport Chemical
Pentamide 2 -- Heyden Newport Chemical
Phosphorane -- American Potash & Chemical Corporation
Plaskon 8200P (nylon type 6) -- Allied Chemical Corporation
Polyetherdiamine L-2000 -- Union Carbide Chemical Company
PRDA (8060NT, phenoxy-8) -- Union Carbide Chemical Company
Prebond 700 -- Bloomingdale Rubber Company
Pyrostop E-100 -- Richardson Company
RCI #8037 -- Reichhold Chemical Corporation
Resin 3135 -- Narmco Materials Division, Telecomputing Corporation
Resin 3135/7111 -- Narmco Materials Division, Telecomputing Corporation
Resin 3147 -- Narmco Materials Division, Telecomputing Corporation
Resin 3170 -- Narmco Materials Division, Telecomputing Corporation
Resin 7343 -- Narmco Materials Division, Telecomputing Corporation
Resin X-310 -- Narmco Materials Division, Telecomputing Corporation
Santocel C -- Monsanto Chemical Company
Saran 723 -- Dow Chemical Company
Shell Curing Agent U -- Shell Chemical Company
Silastic 140, 731 & Q-9-0002A/B, 1200 Primer -- Dow Chemical Company
Syntex 3398 -- Jones-Dabney
T-1 Curing Agent -- Shell Chemical Company
Tedlar -- DuPont
Teflon 7 -- E. I. duPont deNemours & Company Inc.
Teflon FEP -- E. I. duPont deNemours & Company Inc.
Teflon FEP film, etches -- W. S. Shamban & Company
Teflon FEP Type A -- E. I. duPont deNemours & Company
Teflon FEP Type 544 -- E. I. duPont deNemours & Company
Teflon TFE -- R. S. Hughes Co. Inc. 4515 Alger St. Los Angeles 39, Calif.
Teflon TFE powder, etches -- W. S. Shamban & Company
Thiokol FA -- Thiokol Chemical Corporation
Thiokol LP 3 -- Thiokol Chemical Corporation
TP-440 polyol -- Wyandotte
TP-740 -- Wyandotte
UR80T -- Seiberling Rubber Company
Versamid 115 -- General Mills
Versamid 125 -- General Mills
Versamid 140 -- General Mills
Vibrin 136 A -- U. S. Rubber
Viton A-HV -- DuPont
Webril 1514-M -- Kendal Mills
X-295 to X-304 -- Narmco Research & Development, a Division of Telecomputing Corp.
Zytel 31 (nylon type 6, 10) -- DuPont
Zytel 61 -- DuPont
25P6/A1100 Prime -- Narmco Research & Development, a Division of Telecomputing Corp.

XXIII. COMPLETE SPECIFICATIONS FOR THE DEVELOPED ADHESIVES

A. ADHESIVE A. Specifications and Qualification

1. Uses:

For bonding clips, brackets, etc., to skin portions of fuel and oxidizer containers and other related components for launch vehicles. The adhesive is readily adaptable to field use by technicians having little or no experience in plastics technology. Surface preparations can be simple, bonding and curing can be accomplished under ambient conditions at contact pressure, and the resultant bonded assemblies are applicable when submerged in cryogens such as liquid nitrogen and liquid hydrogen.

Note: This adhesive should not be used where it will be directly exposed to liquid oxygen.

2. Description:

Adhesive A, also designated as Narmco Resin 3170 and Curing Agent 7133, is a two-part system consisting of a nylon-filled epoxy resin and a nylon-filled polyamide curing agent, respectively.

3. Surface Preparations:

Chemical etches are to be preferred over all mechanical methods. A chemical etch can be prepared for field application. Mechanical methods such as solvent degreasing, sanding, and sandblasting should only be used as a last resort. Surfaces should be bonded as soon after cleaning as possible.

a. Chemical Etch for Aluminum Alloys

Sodium Dichromate	30	Parts
Distilled Water	170	"
Concentrated Sulfuric Acid	50	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 5-10 minutes in the above solution maintained at 150-160°F. Rinse with tap water and then with distilled water. Oven dry at 150°F.

b. Field Chemical Etch for Aluminum

Sodium Dichromate	30	Parts
Distilled Water	50	"
Concentrated Sulfuric Acid	50	"
Silica Gel (Santocel C)	10	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the heavy paste etchant on all surfaces to be bonded and allow to remain 50 minutes. Wash down with a stream of running tap water to remove all traces of etchant. Air dry.

c. <u>Chemical Etch for Stainless Alloys</u>

<u>Solution #1</u>			<u>Solution #2</u>		
Hydrochloric Acid (35%)	100	Parts	Sulfuric Acid (98%)	100	Parts
Hydrogen Peroxide (30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Distilled Water	90	"			

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10 minutes in Solution #1 maintained at 150°F. Rinse with tap water and distilled water. Oven dry at 150°F. Immerse 5-10 minutes in solution #2 maintained at 140-160°F. Repeat rinsing and drying procedures.

d. <u>Field Chemical Etch for Stainless</u>

<u>Paste #1</u>			<u>Paste #2</u>		
Hydrochloric Acid (35%)	100	Parts	Sulfuric Acid (98%)	100	Parts
Hydrogen Peroxide (30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Silica Gel(Santocel C)	15.5	"	Silica Gel(Santocel C)	15	

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the Paste #1 on all surfaces to be bonded and allow to remain 40 minutes. Wash down with a stream of running water to remove all traces of etchant. Air dry. Paint the Paste #2 on all surfaces to be bonded and allow to remain 40 minutes. Repeat rinsing and drying procedures.

e. <u>Chemical Etch for Titanium</u>

Concentrated Nitric Acid	30	Parts
Hydrofluoric Acid	5	"
Water	100	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10-15 minutes in above solution maintained at 100-125°F. Rinse with tap water followed by distilled water. Oven dry at 150°F.

4. Mixing: Formulation

       Nylon-filled Epoxy Constituent (Resin 3170) . . . . 50 parts
       by Weight or Volume.
       Nylon-filled Polyamine Constituent (Resin 7133) . . . . . . 50 parts
       by Weight or Volume.

Just prior to application, combine the two reactive constituents in equal parts by weight or volume. A maximum of one pound of combined adhesive is suggested to prevent exotherm and shortened pot life. Good blending can be attained by hand-mixing with a spatula until the entire mass takes on a creamy, homogeneous appearance. The average pot or working life is 1-1/2 to 2 hours at 75°F.

5. Application:

Trowel or squeeze the mixed adhesive to a thickness of approximately 5-mils on both cleaned adherend surfaces to be bonded. Thickness may be reduced or increased on smaller or larger parts, respectively, to facilitate obtaining the final total glueline thickness. Assemble the surfaces to be bonded and apply sufficient pressure to yield a final glueline thickness of 3-5 mils. A variety of suitable jigs and clamps may be used to apply a positive contact pressu e to the assembly until the time necessary to develop required strength has elapsed. For bonding overhead or vertical surfaces, masking tape may be used to dam-up the flash areas of the bonded area to prevent flow-out of the adhesive.

6. Curing:

Gellation of Adhesive A will occur in about 6 hours at ambient temperature. In general, optimum room temperature strength is attained after 22 hours cure at ambient temperature; low temperature strength develops about one-third as fast, not reaching optimum until about four days after bonding.

Curing time may be markedly reduced by raising the temperature. For example, a 1/2-hour cure at 200°F is approximately equivalent to four days cure at 75°F.

7. **Physical Properties**

a. Tensile Shear Strength, psi (.064" alloy with 1/2" overlap. Tested per MIL-A-5090D)

	7075-T6 Aluminum	301-1/2 Hard Stainless	AMS 4910 Titanium
-423°F	2500		
-320	2700	650	1300
-67	3700		
RT	3100	2400	2400
+125	1500		
+180	500		

b. Tee Peel Strength, lbs/1" (.020" 7075T6 Bare aluminum alloy 1" x 12" strips with total overlap. Tested at head travel of 2"/min)

-423	3.0
-320	3.5
-67	4.0
RT	3.9
+125	9.0
+180	2.0

c. Coefficient of Linear Thermal Expansion, in/in °F x 10^5, (Annual Report, Contract NAS8-1565, page 10)

Temperature Range
from -320 to +32°F 3.17

d. Impact Strength, ft-lbs/1 in^2 (7075T6 Bare aluminum alloy. Federal Test Method Standard No. 175. Methods 1051 and 1051.1-T)

-320°F	10.7
RT	14.4

e. Butt Tensile Strength, psi (Federal Test Method Standard No. 175, Method 1011.1)

-423°F	5700	RT	3200
-320	5400	+125°F	1250
-67	3900	+180	750

f. Compressive Strength, psi (Compressive load sustained by joint and dimensional changes)

-320°F	RT
60,000 psi - No Change	60,000 psi - No Change

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g. Mechanical Shock at -423°F

      50 G, 1/2 Sine, 6 Shocks, 7 Milliseconds - "GO"
      100 G,   "   , 1 Shock - "NO GO"

h. LOX Compatibility

    This adhesive should not be used where it will be directly exposed
    to liquid oxygen.

B. **ADHESIVE B.** **Specifications and Qualification**

1. **Uses:**

   For bonding clips, brackets, etc., to skin portions of fuel and oxidizer containers and other related components for launch vehicles. The adhesive is readily adaptable to field use by technicians having little or no experience in plastics technology. Surface preparations can be simple, bonding and curing can be accomplished under ambient conditions at contact pressure, and the resultant bonded assemblies are applicable when submerged in cryogens such as liquid nitrogen and liquid hydrogen.

   Note: This adhesive should not be used where it will be directly exposed to liquid oxygen.

2. **Description:**

   Adhesive B is a three-part composite system consi ting of two substrate films of 1-mil Teflon FEP, Type 544 adhered and laminated between adherends with Narmco Resin 3135 and Curing Agent 7111, an epxoy and polyamide adhesive, respectively.

3. **Surface Preparations:**

   Chemical etches are to be preferred over all mechanical methods. A chemical etch can be prepared for field application. Mechanical methods such as solvent degreasing, sanding, and sandblasting should only be used as a last resort. Surfaces should be bonded as soon after cleaning as possible.

   a. **Chemical Etch for Aluminum Alloys**

Sodium Dichromate	30	Parts
Distilled Water	170	"
Concentrated Sulfuric Acid	50	"

   Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 5-10 minutes in the above solution maintained at 150-160°F. Rinse with tap water and then with distilled water. Oven dry at 150°F.

   b. **Field Chemical Etch for Aluminum**

Sodium Dichromate	30	Parts
Distilled Water	50	"
Concentrated Sulfuric Acid	50	"
Silica Gel (Santocel C)	10	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the heavy paste etchant on all surfaces to be bonded and allow to remain 50 minutes. Wash down with a stream of running tap water to remove all traces of etchant. Air dry.

c. Chemical Etch for Stainless Alloys

Solution #1			Solution #2		
Hydrochloric Acid(35%)	100	Parts	Sulfuric Acid (98%)	100	Parts
Hydrogen Peroxide(30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Distilled Water	90	"			

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10 minutes in Solution #1 maintained at 150°F. Rinse with tap water and distilled water. Oven dry at 150°F. Immerse 5-10 minutes in solution #2 maintained at 140-160°F. Repeat rinsing and drying procedures.

d. Field Chemical Etch for Stainless

Paste #1			Paste #2		
Hydrochloric Acid(35%)	100	Parts	Sulfuric Acid (98%)	100	Parts
Hydrogen Peroxide(30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Silica Gel(Santocel C)	15.5	"	Silica Gel(Santocel C)	15	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the Paste #1 on all surfaces to be bonded and allow to remain 40 minutes. Wash down with a stream of running water to remove all traces of etchant. Air dry. Paint the Paste #2 on all surfaces to be bonded and allow to remain 40 minutes. Repeat rinsing and drying procedures.

e. Chemical Etch for Titanium

Concentrated Nitric Acid	30	Parts
Hydrofluoric Acid	5	"
Water	100	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10-15 minutes in above solution maintained at 100-125°F. Rinse with tap water followed by distilled water. Oven dry at 150°F.

4. **Mixing**:

       Expoxy Constituent (Resin 3135) . . . . 50 Parts
by Weight or Volume.
Polyamide Constituent (Curing Agent 7111) . . . . 50 Parts
by Weight or Volume.
1-Mil Teflon FEP, Type 544 . . . . Two substrate Films.

Just prior to application, combine Resin 3135 with Curing Agent 7111 in
the recommended ratio. A maximum of one pound of combined adhesive is
suggested to prevent excessive exotherm and shortened pot life. Good
blending can be attained by hand-mixing with a spatula until the entire
mass takes on a creamy, homogeneous appearance. The average pot or
working life is 1-1/2 - 2 hours at 75°F.

5. **Application**:

Cut the two substrate films of 1-mil Teflon FEP, Type 544, large
enough to underlay the adherend bonding area and extend 1/4" in all
directions. Trowel or squeeze the prepared adhesive to a thickness of
approximately 2 mils on both adherend surfaces to be bonded. Trowel
or squeeze both sides of each of the two films to a thickness of approxi-
mately 2 mils with the prepared adhesive. Assemble the prepared sur-
faces to be bonded with the two substrate films laminated between.
Apply sufficient pressure to yield a glueline thickness of 5-8 mils. A
variety of suitable jigs and clamps may be used to apply a positive
contact pressure to the assembly until time necessary to develop required
strength has elapsed. For bonding overhead or vertical surfaces, masking
tape may be used to dam-up the flash area of the bonded area to prevent
flow-out of the adhesive.

6. **Curing**:

Gellation of Adhesive B will occur in about 6 hours at ambient temper-
ature. In general, optimum room and low temperature strengths are
attained after 22 hours cure at ambient temperature.

Curing time may be markedly reduced by raising the temperature. For
example, a 1/2-hour cure at 200°F is approximately equivalent to 22 hours
cure at 75°F.

7. **Physical Properties:**

a. Tensile Shear Strength, psi (.064" alloy with 1/2" overlap. Tested per MIL-A-5090D)

	7075-T6 Aluminum	301-1/2 Hard Stainless	AMS 4910 Titanium
-423°F	5300		
-320	5000	1200	980
-67	3800		
RT	1900	700	1580
+125	1300		
+180	700		

b. Tee Peel Strength, lbs/1" (.020" 7075T6 Bare aluminum alloy 1" x 12" strips with total overlap. Tested at head travel of 2"/min)

-423	6.0
-320	9.0
-67	7.0
RT	4.0
+125	8.0
+180	2.0

c. Impact Strength, ft-lbs/1 in^2 (7075T6 Bare aluminum alloy. Federal Test Method Standard No. 175, Methods 1051 and 1051.1-T)

-320°F	0.6
RT	2.6

d. Butt Tensile Strength, psi (Federal Test Method Standard No. 175, Method 1011.1)

-423°F	.9200	RT	.1900
-320	.6100	+125°F. . . .	.1600
-67	.3100	+180°F. . . .	.1000

e. Compressive Strength, psi (Compressive load sustained by joint and dimensional changes)

-320°F	RT
60,000 psi - No Change	60,000 psi - No Change

f. Mechanical Shock at -423°F

    100 G, 1/2 Sine, 6 Shocks - "GO"

    (50 G - inconclusive)

g. LOX Compatibility

    This adhesive should not be used where it will be directly exposed
    to liquid oxygen.

C. **ADHESIVE C.**   **Specifications and Qualification**

1. **Uses:**

   For bonding clips, brackets, etc., to skin portions of fuel and
   oxidizer containers and other related components for launch vehicles.
   The adhesive is readily adaptable to field use by technicians having
   little or no experience in plastics technology. Surface preparations
   can be simple, bonding and curing can be accomplished under ambient
   conditions at contact pressure, and the resultant bonded assemblies are
   applicable when submerged in cryogens such as liquid nitrogen and liquid
   hydrogen.

   Note: This adhesive should not be used where it will be directly exposed
          to liquid oxygen.

2. **Description:**

   Adhesive C is a two-part system consisting of Adiprene L-100 (also
   designated as Narmco Resin 7343) polyurethane elastomer and Moca (also
   designated as Narmco Curing Agent 7139).

3. **Surface Preparations:**

   Chemical etches are to be preferred over all mechanical methods. A
   chemical etch can be prepared for field application. Mechanical methods
   such as solvent degreasing, sanding, and sandblasting should only be
   used as a last resort. Surfaces should be bonded as soon after cleaning
   as possible.

   a. **Chemical Etch for Aluminum Alloys**

Sodium Dichromate	30	Parts
Distilled Water	170	"
Concentrated Sulfuric Acid	50	"

   Degrease all surfaces with a clean cloth saturated with methyl ethyl
   ketone. Immerse 5-10 minutes in the above solution maintained at
   150-160°F. Rinse with tap water, then with distilled water. Oven
   dry at 150°F.

   b. **Field Chemical Etch for Aluminum**

Sodium Dichromate	30	Parts
Distilled Water	50	"
Concentrated Sulfuric Acid	50	"
Silica Gel (Santocel C)	10	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the heavy paste etchant on all surfaces to be bonded and allow to remain 50 minutes. Wash down with a stream of running tap water to remove all traces of etchant. Air dry.

c. Chemical Etch for Stainless Alloys

Solution #1			Solution #2		
Hydrochloric Acid(35%)	100	Parts	Sulfuric Acid(98%)	100	Parts
Hydrogen Peroxide(30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Distilled Water	90	"			

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10 minutes in Solution #1 maintained at 150°F. Rinse with tap water and distilled water. Oven dry at 150°F. Immerse 5-10 minutes in solution #2 maintained at 140-160°F. Repeat rinsing and drying procedures.

d. Field Chemical Etch for Stainless

Paste #1			Paste #2		
Hydrochloric Acid (35%0	100	Parts	Sulfuric Acid (98%)	100	Parts
Hydrogen Peroxide (30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Silica Gel (Santocel C)	15.5	"	Silica Gel(Santocel C)	15	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the Paste #1 on all surfaces to be bonded and allow to remain 40 minutes. Wash down with a stream of running water to remove all traces of etchant. Air dry. Paint the Paste #2 on all surfaces to be bonded and allow to remain 40 minutes. Repeat rinsing and drying procedures.

e. Chemical Etch for Titanium

Concentrated Nitric Acid	30	Parts
Hydrofluoric Acid	5	"
Water	100	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10-15 minutes in above solution maintained at 100-125°F. Rinse with tap water followed by distilled water. Oven dry at 150°F.

4. **Mixing**:

> Adiprene L-100 (Narmco Resin 7343) . . . . . . 100 Parts by Weight
> Moca (Narmco Curing Agent 7139). . . . . 11 Parts by Weight

Just prior to application, weigh the required amounts of reactive ingredients (a 2% weight error can be tolerated). Melt the required amount of Curing Agent 7139 at 250°F +25°F. Using a spatula, stir this into Resin 7343 at room temperature. A clear, homogeneous solution should result. A maximum of one pound of combined adhesive is suggested to prevent excessive exotherm and shortened pot life. The average pot life should be about 8 hours at 75°F. Manufacturer's storage and handling precautions for Resin 7343 should be followed.

5. **Application**:

Trowel or squeeze the prepared adhesive to a thickness of approximately 5 mils on both adherend surfaces to be bonded. Assemble the prepared surfaces and apply sufficient pressure to yield a glueline thickness of 3-5 mils. A variety of suitable jigs and clamps may be used to apply a positive contact pressure to the assembly until time necessary to develop required strength has elapsed. For bonding overhead or vertical surfaces, masking tape may be used to dam-up the flash areas of the bonded area to prevent flow-out of the adhesive.

6. **Curing**:

Gellation of the adhesive will occur in about 24 hours at ambient temperature. In general, optimum room temperature and low temperature strengths are attained after 3-days cure at 75°F. The low temperature strength develops about three times as fast as the ambient strength. The optimum low temperature strength is about three times that of the optimum ambient temperature strength.

Curing time may be markedly reduced to 4 hours at 158°F, 3 hours at 212°F, 1 hour at 285°F, or 30 minutes at 320°F.

7. **Physical Properties**:

a. Tensile Shear Strength, psi (.064" alloy with 1/2" overlap. Tested per MIL-A-5090D)

	7075-T6 Aluminum
-423°F	8000
-320	5000
-67	4600
RT	1600
+125	700
+180	450

b. Tee Peel Strength, lbs/1" (.020" 7075T6 Bare aluminum alloy 1"x12" strips with total overlap. Tested at head travel of 2"/min)

-423°F	26.0
-320	33.0
-67	22.5
RT	11.3
+125	9.0
+180	10.0

c. Impact Strength, ft-lbs/1 in^2 (7075T6 Bare aluminum alloy. Federal Test Method Standard No. 175, Methods 1051 and 1051.1-T)

-320°F	13.15
RT	12.57

d. Butt Tensile Strength, psi (Federal Test Method Standard No. 175, Method 1011.1)

-423°F . . . 7600		RT . . . 1800
-320 . . . 6200		+125 . . . 1000
-67 . . . 5800		+180 . . . 600

e. Compressive Strength, psi (Compressive load sustained by joint and dimensional changes)

-320°F	RT
60,000 psi - No Change	60,000 psi - No Change

f. Mechanical Shock at -423°F, "Go" or "No Go" after six shocks at 100 G, 1/2 sine wave, and 6 milliseconds duration)

50 G, 1/2 Sine, 6 Shocks, 7 Milliseconds - "GO"
100 G, 1/2 Sine, 6 Shocks, - "GO"

g. LOX Compatibility

This adhesive should not be used where it will be directly exposed to liquid oxygen.

D. **ADHESIVE D.** **Specifications and Qualification**

1. **Uses:**

   For bonding clips, brackets, etc., to skin portions of fuel and oxidizer
   containers and other related components for launch vehicles. The
   adhesive is readily adaptable to field use by technicians having little
   or no experience in plastics technology. Surface preparations can be
   simple, bonding and curing can be accomplished under ambient conditions
   at contact pressure, and the resultant bonded assemblies are applicable
   when submerged in cryogens such as liquid nitrogen and liquid hydrogen.

   Note: This adhesive should not be used where it will be directly exposed
   to liquid oxygen.

2. **Description:**

   Adhesive D is a two-part system consisting of Adiprene LD-167 (also
   designated as Narmco Resin X-310) polyurethane elastomer and Moca (also
   designated as Curing Agent 7139).

3. **Surface Preparations:**

   Chemical etches are to be prepared over all mechanical methods. A
   chemical etch can be prepared for field application. Mechanical methods
   such as solvent degreasing, sanding, and sandblasting should only be
   used as a last resort. Surfaces should be bonded as soon after cleaning
   as possible.

   a. **Chemical Etch for Aluminum Alloys**

Sodium Dichromate	30	Parts
Distilled Water	170	"
Concentrated Sulfuric Acid	50	"

   Degrease all surfaces with a clean cloth saturated with methyl
   ethyl ketone. Immerse 5-10 minutes in the above solution maintained
   at 150-160°F. Rinse with tap water, then with distilled water.
   Oven dry at 150°F.

   b. **Field Chemical Etch for Aluminum**

Sodium Dichromate	30	Parts
Distilled Water	50	"
Concentrated Sulfuric Acid	50	"
Silica Gel (Santocel C)	10	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the heavy paste etchant on all surfaces to be bonded and allow to remain 50 minutes. Wash down with a stream of running tap water to remove all traces of etchant. Air dry.

c. Chemical Etch for Stainless Alloys

Solution #1			Solution #2		
Hydrochloric Acid(35%)	100	Parts	Sulfuric Acid(98%)	100	Parts
Hydrogen Peroxide(30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Distilled Water	90	"			

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10 minutes in Solution #1 maintained at 150°F. Rinse with tap water and distilled water. Oven dry at 150°F. Immerse 5-10 minutes in solution #2 maintained at 140-160°F. Repeat rinsing and drying procedures.

d. Field Chemical Etch for Stainless

Paste #1			Paste #2		
Hydrochloric Acid(35%)	100	Parts	Sulfuric Acid(98%)	100	Parts
Hydrogen Peroxide(30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Silica Gel(Santocel C)	15.5	"	Silica Gel(Santocel C)	15	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the Paste #1 on all surfaces to be bonded and allow to remain 40 minutes. Wash down with a stream of running water to remove all traces of etchant. Air dry. Paint the Paste #2 on all surfaces to be bonded and allow to remain 40 minutes. Repeat rinsing and drying procedures.

e. Chemical Etch for Titanium

Concentrated Nitric Acid	30	Parts
Hydrofluoric Acid	5	"
Water	100	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10-15 minutes in above solution maintained at 100-125°F. Rinse with tap water followed by distilled water. Oven dry at 150°F.

4. Mixing:

    Adiprene LD-167 (Narmco Resin X-310) . . . . . 100 Parts by Weight
    Moca (Narmco Curing Agent 7139) . . . . 11 Parts by Weight

Just prior to application, weigh the required amounts of reactive
ingredients (a 2% weight error can be tolerated). Melt the required
amount of Curing Agent 7139 at 250°F + 25°F. Stir into Resin X-310 at
room temperature using a spatula. A clear, homogeneous solution should
result. A maximum of one pound of combined adhesive is suggested to
prevent excessive exotherm and shortened pot life. The average pot life
should be about 8 hours at 75°F. Manufacturer's storage and handling
precautions for Resin X-310 should be followed.

5. Application:

Trowel or squeeze the prepared adhesive to a thickness of approximately
5 mils on both adherend surfaces to be bonded. Assemble the prepared
surfaces and apply sufficient pressure to yield a glueline thickness
of 3-5 mils. A variety of suitable jigs and clamps may be used to apply
a positive contact pressure to the assembly until time necessary to
develop required strength has elapsed. For bonding overhead or vertical
surfaces, masking tape may be used to dam-up the flash areas of the
bonded area to prevent flow-out of the adhesive.

6. Curing:

Gellation of the adhesive will occur in about 24 hours at ambient temper-
ature. In general, optimum room temperature and low temperature strengths
are attained after 3-days cure at 75°F. The low temperature strength
develops about three times as fast as the ambient strength. The optimum
low temperature strength is about three times that of the optimum ambient
temperature strength.

Curing time may be markedly reduced to 4 hours at 158°F, 3 hours at 212°F,
1 hour at 285°F, or 30 minutes at 320°F.

7. **Physical Properties:**

   a. Tensile Shear Strength, psi (.064" alloy with 1/2" overlap. Tested per MIL-A-5090D)

	7075-T6 Aluminum	301 1/2-Hard Stainless
-423°F	6700	
-320	5100	3500
-67	5000	
RT	1900	680
+125	850	
+180	350	

   b. Tee Peel Strength, lbs/1" (.020" 7075T6 Bare aluminum alloy 1"x12" strips with total overlap. Tested at head travel of 2" min)

-423°F	26.0
-320	22.5
-67	9.5
RT	30.0
+125	9.0
+180	9.5

   c. Impact Strength, ft-lbs/1 in^2 (7075T6 Bare aluminum alloy. Federal Test Method Standard No. 175, Methods 1051 and 1051.1-T)

   | -320°F . . . . | 1.10 |
   | RT . . . . | 3.07 |

   d. Butt Tensile Strength, psi (Federal Test Method Standard No. 175, Method 1011.1)

-423°F . . .	6800	RT . . .	1900
-320 . . .	7700	+125°F. . .	820
-67 . . .	6300	+180°F. . .	750

   e. Mechanical Shock at -423°F, "Go" or "No Go" after six shocks at 100 G, 1/2 sine wave, and 6 milliseconds duration)

      100 G, 1/2 Sine, 6 Shocks - "GO"

   f. LOX Compatibility

      This adhesive should not be used where it will be directly exposed to liquid oxygen.

E. ADHESIVE E. Specifications and Qualification

1. Uses:

For bonding clips, brackets, etc., to skin portions of fuel and oxidizer containers and other related components for launch vehicles. The adhesive is readily adaptable to field use by technicians having little or no experience in plastics technology. Surface preparations can be simple, bonding and curing can be accomplished under ambient conditions at contact pressure, and the resultant bonded assemblies are applicable when submerged in cryogens such as liquid nitrogen and liquid hydrogen.

Note: This adhesive should not be used where it will be directly exposed to liquid oxygen.

2. Description:

Adhesive E is a three-part system consisting of Adiprene L-100 (also designated as Narmco Resin 7343), polyurethane elastomer and Moca (also designated as Narmco Curing Agent 7139), and 181-112 glass fabric.

3. Surface Preparations:

Chemical etches are to be preferred over all mechanical methods. A chemical etch can be prepared for field application. Mechanical methods such as solvent degreasing, sanding, and sandblasting should only be used as a last resort. Surfaces should be bonded as soon after cleaning as possible.

a. Chemical Etch for Aluminum Alloys

Sodium Dichromate	30	Parts
Distilled Water	170	"
Concentrated Sulfuric Acid	50	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 5-10 minutes in the above solution maintained at 150-160°F. Rinse first with tap water, then with distilled water. Oven dry at 150°F.

b. Field Chemical Etch for Aluminum

Sodium Dichromate	30	Parts
Distilled Water	50	"
Concentrated Sulfuric Acid	50	"
Silica Gel (Santocel C)	10	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the heavy paste etchant on all surfaces to be bonded and allow to remain 50 minutes. Wash down with a stream of running tap water to remove all traces of etchant. Air dry.

c. Chemical Etch for Stainless Alloys

Solution #1

Hydrochloric Acid(35%)	100	Parts
Hydrogen Peroxide(30%)	4	"
Formalin (40%)	20	"
Distilled Water	90	"

Solution #2

Sulfuric Acid(98%)	100	Parts
Sodium Dichromate	10	"
Distilled Water	30	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10 minutes in Solution #1 maintained at 150°F. Rinse with tap water and distilled water. Oven dry at 150°F. Immerse 5-10 minutes in solution #2 maintained at 140-160°F. Repeat rinsing and drying procedures.

d. Field Chemical Etch for Stainless

Paste #1

Hydrochloric Acid(35%)	100	Parts
Hydrogen Peroxide(30%)	4	"
Formalin (40%0	20	"
Silica Gel(Santocel C)	15.5	"

Paste #2

Sulfuric Acid (98%)	100	Parts
Sodium Dichromate	10	"
Distilled Water	30	"
Silica Gel(Santocel C)	15	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the Paste #1 on all surfaces to be bonded and allow to remain 40 minutes. Wash down with a stream of running water to remove all traces of etchant. Air dry. Paint the Paste #2 on all surfaces to be bonded and allow to remain 40 minutes. Repeat rinsing and drying procedures.

e. Chemical Etch for Titanium

Concentrated Nitric Acid	30	Parts
Hydrofluoric Acid	5	"
Water	100	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10-15 minutes in above solution maintained at 100-125°F. Rinse with tap water followed by distilled water. Oven dry at 150°F.

4. Mixing:

>   Adiprene L-100 (Narmco Resin 7343) . . . . 100 Parts by Weight
>   Moca (Narmco Curing Agent 7139) . . . . 11 Parts by Weight

Just prior to application, weigh the required amounts of reactive
ingredients (2 2% weight error can be tolerated). Melt the required
amount of Curing Agent 7139 at 250°F +25°F. Stir this into Resin 7343
at room temperature using a spatula. A clear, homogeneous solution
should result. A maximum of one pound of combined adhesive is
suggested to prevent excessive exotherm and shortened pot life. The
average pot life should be about 8 hours at 75°F. Manufacturer's
storage and handling precautions for Resin 7343 should be followed.

5. Application:

Trowel or squeeze the prepared adhesive to a thickness of approximately
5 mils on both adherend surfaces to be bonded. Trowel or squeeze the
prepared adhesive into a single layer of 181-112 glass fabric taking
care that the fabric is well-impregnated. Assemble the prepared sur-
faces with impregnated fabric between and apply sufficient pressure to
yield a glueline thickness of 8-12 mils. A variety of suitable jigs
and clamps may be used to apply a positive contact pressure to the
assembly until time necessary to develop required strength has elapsed.
For bonding overhead or vertical surfaces, masking tape may be used to
dam-up the flash areas of the bonded area to prevent flow-out of the
adhesive.

6. Curing:

Gellation of the adhesive will occur in about 24 hours at ambient temper-
ature. In general, optimum room temperature and low temperature strengths
are attained after 3-days cure at 75°F. The low temperature strength
develops about three times as fast as the ambient strength. The optimum
low temperature strength is about three times that of the optimum
ambient temperature strength.

Curing time may be markedly reduced to 4 hours at 158°F, 3 hours at
212°F, 1 hour at 285°F, or 30 minutes at 320°F.

7. Physical Properties:

a. Tensile Shear Strength, psi (.064" alloy with 1/2" overlap. Tested per MIL-A-5090D)

	7075-T6 Aluminum	301 1/2-Hard Stainless
-423°F	6500	
-320	5200	3600
-67	4500	
RT	1000	600
+125	660	
+180	400	

b. Tee Peel Strength, lbs/1" (.020" 7075T6 Bare aluminum alloy 1"x12" strips with total overlap. Tested at head travel of 2"/min)

-243°F	44.0
-320	46.0
-67	14.0
RT	20.0
+125	13.0
+180	11.0

c. Impact Strength, ft-lbs/1 in^2 (7075T6 Bare aluminum alloy. Federal Test Method Standard No. 175, Methods 1051 and 1051.1-T)

-320°F	14.1
RT	3.07

d. Butt Tensile Strength, psi (Federal Test Method Standard No. 175, Method 1011.1)

-423°F	6200	RT	800
-320	5900	+125°F	580
-67	4100	+180	470

e. Mechanical Shock at -423°F, "Go" or "No Go" after six shocks at 100 G, 1/2 sine wave, and 6 milliseconds duration

100 G, 1/2 Sine, 6 Shocks, 6 Milliseconds - "NO GO"

f. LOX Compatibility

This adhesive should not be used where it will be directly exposed to liquid oxygen.

F. **ADHESIVE F.** Specifications and Qualification

1. Uses:

   For bonding, clips, brackets, etc., to skin portions of fuel and
   oxidizer containers and other related components of launch vehicles.
   The adhesive is adaptable to field use by technicians having little or
   no experience in plastics technology. Surface preparations can be
   simple, and the resultant bonded assemblies are applicable when sub-
   merged in cryogens such as liquid oxygen, liquid nitrogen, and liquid
   hydrogen.

2. Description:

   Adhesive F is a single-part system consisting of Dupont's Teflon FEP
   film (5 mil) processed by fusion techniques.

3. Surface Preparations:

   Only those adherends which are compatible with 700°F should be considered.
   Chemical etches are to be preferred over all mechanical methods. A
   chemical etch can be prepared for field application. Mechanical methods
   such as solvent degreasing, sanding, and sandblasting should only be used
   as a last resort. Surfaces should be bonded as soon after cleaning as
   possible.

   a. Chemical Etch for Stainless Alloys

Solution #1			Solution #2		
Hydrochloric Acid (35%)	100	Parts	Sulfuric Acid (98%)	100	Parts
Hydrogen Peroxide (30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Distilled Water	90	"			

   Degrease all surfaces with a clean cloth saturated with methyl ethyl
   ketone. Immerse 10 minutes in Solution #1 maintained at 150°F.
   Rinse with tap water and distilled water. Oven dry at 150°F.
   Immerse 5-10 minutes in solution #2 maintained at 140-160°F. Repeat
   rinsing and drying procedures.

   b. Field Chemical Etch for Stainless

Paste #1			Paste #2		
Hydrochloric Acid (35%)	100	Parts	Sulfuric Acid (98%)	100	Parts
Hydrogen Peroxide (30%)	4	"	Sodium Dichromate	10	"
Formalin (40%)	20	"	Distilled Water	30	"
Silica Gel (Santocel C)	15.5	"	Silica Gel (Santocel C)	15	"

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Paint the Paste #1 on all surfaces to be bonded and allow to remain 40 minutes. Wash down with a stream of running water to remove all traces of etchant. Air dry. Paint the Paste #2 on all surfaces to be bonded and allow to remain 40 minutes. Repeat rinsing and drying procedures.

c. **Chemical Etch for Titanium**

Concentrated Nitric Acid	30 Parts
Hydrofluoric Acid	5 "
Water	100 "

Degrease all surfaces with a clean cloth saturated with methyl ethyl ketone. Immerse 10-15 minutes in above solution maintained at 100-125°F. Rinse with tap water, then with distilled water. Oven dry at 150°F.

4. **Application and Cure:**

Cut one piece of Teflon FEP film (5-mils thickness) to extend approximately 1/4" beyond edges of surfaces to be bonded. Assemble the prepared surfaces with film between and raise the temperature of the assembly to 700°F. Suitable pressure should be applied to yield a glue-line thickness of 3-5 mils. Cool the assembly under pressure.

For field application, the 700°F temperature can be attained by RF, resistance, or other electrical heating techniques. Exothermic tape materials, such as Narmco's Exoflux, when applied to the outer surfaces or extremities of bonding assemblies, can be used to give closely controlled temperatures after ignition.

5. **Physical Properties:**

a. Tensile Shear Strength, psi (.050 alloy with 1/2" overlap. Tested per MIL-A-5090D)

	17-7 PH Stainless
-423°F	5300
-320	4000
-67	3100
RT	1400
+125	930
+180	820

b. Tee Peel Strength, lbs/1" (.020" 17-7 PH stainless 1" x 12" strips with total overlap. Tested at a head travel of 2"/min).

$$
\begin{array}{ll}
-423°F & \ldots \ldots \ldots \quad -- \\
-320 & \ldots \ldots \ldots 51.0 \\
-67 & \ldots \ldots \ldots 18.5 \\
RT & \ldots \ldots \ldots 10.0 \\
+125 & \ldots \ldots \ldots \quad 5.5 \\
+180 & \ldots \ldots \ldots \quad 4.5
\end{array}
$$

c. LOX Compatibility

This adhesive is reported to be insensitive when it is used in direct contact with liquid oxygen.

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XXIV. SUMMARY

The literature survey and initial adhesive evaluation tests demonstrated the superiority of the nylon-epoxy adhesive systems for cryogenic applications. The commercially available forms required 25 pounds per square inch curing pressure and 350°F for cure. Various attempts were made to reduce these curing requirements in line with the target objectives of the program. These attempts included synthesis of various nylons, copolymerization and melt combinations of various nylons, and nylon-epoxy coreaction studies. Due to melting point and nylon epoxy compatibility limitations, the target curing objectives were not met by this general approach. The epoxy-nylon coreaction technique came the closest to this end and deserves further consideration.

The effects of fillers were studied using an epoxy-polyamine system which possessed the desired processability, but was, in general, too brittle at cryogenic temperatures. Initial attempts to correlate the coefficient of expansion effects of fillers to adhesive strength and toughness (tee peel) at low temperatures were unsuccessful. Nevertheless, one filler (powdered nylon) did produce a marked improvement in low temperature toughness of the base epoxy-polyamine system. One nylon (Zytel 61) performed better than other commercial grades of those synthesized in this program. This nylon-filled, epoxy-polyamine system, Adhesive A, was selected as one adhesive for further study and evaluation in view of its ease of processability, excellent moderately low temperature strength properties, and fair strength and toughness at low temperature. Epoxy-polyamine ratio studies did not improve upon this basic system.

The filler approach was expanded to include film substrate composites composed of the epoxy-polyamine adhesive with extensible film interlayers. Various types of films were evaluated where elongation at low temperature was considered as a desirable property. Films included fluorinated and chlorinated polymers and elastomers, nylon, Mylar, and polyurethanes, as well as metals such as lead, copper, cadmium, etc. Due either to modulus or adhesion problems, many of these films detracted from the basic adhesive strength and toughness of the epoxy-polyamine. The fluorocarbon or halo-fluorocarbon films noticeably improved both strength and toughness at -320°F. Films of Teflon fluoroethylene hexafluoro propylene (FEP) contributed the most to peel strength and tensile shear at -320°F of any film system studied. These substrate systems developed the best all-around strength-to-toughness properties over the room to -423°F temperature range of any room temperature curing adhesive evaluated. One of these, Adhesive B, was selected for complete evaluation.

Based upon the initial literature survey and subsequent commercial adhesive evaluations, polyurethane polymers were also included in this study. In general, the polyurethane elastomers were found to exhibit superior strength and toughness characteristics at extremely low temperature when compared to

any of the other adhesives studied. The biggest difficulty with the polyurethanes is their sensitivity to moisture and subsequent blowing or foaming tendency. This results from the gaseous carbon dioxide produced from the isocyanate reaction with moisture in the air. This effect is very pronounced during elevated temperature curing, but minimizes with RT curing. Three poly- urethane elastomer adhesives were selected Adhesives C, D, and E. The first gives an excellent balance of strength and toughness at -423°F, the second gives essentially the same properties but offers faster cure, and the third gives the highest peel strength at -423°F (44 lbs/1") or any adhesive studies.

Only one adhesive, Adhesive F, demonstrated compatibility with liquid oxygen. This adhesive consisted of a fluorocarbon film requiring bonding at temperatures up to 700°F. The strength and toughness characteristics were excellent over a broad temperature range. The high bonding temper- ature could be overcome in field application by RF or resistance heating, exotherm tapes, etc.

Mechanical shock, butt tensile, impact, compression loading, thermal expansion, and other data are also given for these adhesives down to -423°F.

The six selected adhesives demonstrated, in general, an excellent coverage of the target objectives of this program. Their greatest shortcomings were high-temperature strength and, with the exception of Adhesive F, sensitivity to liquid oxygen. The low-temperature strength and toughness of the adhesives compares very favorably with, or exceeds those of, adhesives requiring much more severe bonding conditions than the room temperature, contact pressure curing characteristics of the developed systems.

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surface roughness of the metal substrate to which polymeric films adhere.
"Chemical & Engineering News," Sept. 10, 1962, p. 8.

TABLE OF SYMBOLS AND ABBREVIATIONS

Symbol	Definition
phr	Parts (by weight) of filler, curing agent, etc., per 100 parts (by weight) of resin
pbw	Parts by weight
RT	Room temperature
psi	Pounds per square inch
#	Number
mil	One-thousandth of an inch
hr	Hour
LH_2	Liquid hydrogen
LN_2	Liquid nitrogen
LOX	Liquid oxygen

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